

ABSTRACT

CHENG-KANG LI. The Use of Polycyclic Aromatic Hydrocarbons as Source Signatures in Receptor Modeling. (Under The Direction of Professor Richard M. Kamens)

The identification of combustion sources with polycyclic aromatic hydrocarbons (PAH) source signatures in the chemical mass balance model (CMB) was examined in this study. Three combustion sources, residential wood combustion, gasoline and diesel vehicular emissions, were investigated. Source PAH emissions were characterized and each source emission was expressed as a source pattern with a specific concentration. A normalized concentration method which takes advantage of the pattern characteristic was developed to provide effective separation in two-source conditions. When PAH reactivity is introduced, a CMB model with a continuous stirred tank reactor (CSTR) decay factor (Friedlander 1981) was used for ambient samples. Reasonable predictions were obtained in two case studies in which PAH data exist and source receptor modeling was undertaken using other tracers.

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I. INTRODUCTION

Purpose

The purpose of this report is to explore the use of polycyclic aromatic hydrocarbons (PAH) as organic tracers or source signatures in a receptor model to identify different combustion sources.

Need for research

Over the past two decades, receptor source-apportionment models have been developed to assist in defining control strategies for particulate pollutant. The most widely used receptor model is Chemical Mass Balances (CMB). The basic concept of the CMB model is that composition patterns of emissions from various classes of sources are different enough that one can identify their contributions by measuring concentrations of many species in samples collected at a receptor site.

Trace elements have been used successfully as tracers to identify different kinds of sources, such as: soil, industrial emissions, secondary particulates from coal fired power plants and vehicles emission. Before 1986, Pb and Br were abundant in automotive fuel, and those elements were

effective tracers for automotive emissions. Today in the United States automotive fuel no longer contains significant amounts of Pb and Br, and, therefore, those elements no longer are useful tracers for automotive emissions. In addition, other sources, such as home heating oil combustion, home heating wood combustion, petroleum refinery, also lack effective tracers for source identification. All of the above emissions come from fossil fuels or vegetative materials and contain low or unstable elemental tracers. Thus, different studies have suggested that organic compounds may show some promise as alternatives to trace elements as tracers for source identification (Daisey et al. 1986, Gordon 1988).

Among the characterized organic emissions from different combustion sources, polycyclic aromatic hydrocarbons (PAHs) are often suggested as possible tracers (Daisey et al. 1986, Simoneit 1984). PAHs are produced mainly by high temperature incomplete combustion reactions of organic materials including fossil fuels. Different investigators have suggested that compositional differences in PAH compounds resulting from the combustion of different fuels can be exploited for source identification (Gordon and Bryan 1973, Daisey et al. 1979, Daisey and Lioy 1981).

Although the use of PAH compounds seems reasonable, the progress of organic receptor modeling is still restricted by a lack of knowledge of the atmospheric chemical reactivity

of PAHs. Without this information to estimate the representative PAH signatures for the receptor, the model will fail because of incorrect input data. To avoid a reactivity effect, some ambient studies have used organics as tracers in receptor models during winter months when little degradation in the tracers is predicted (Miguel et al. 1989, Larson et al. 1988).

Controlled outdoor chamber studies at University of North Carolina at Chapel Hill have been used to develop empirical expressions to estimate the decay rate constants of PAH compounds on atmospheric wood soot particles. The reaction rates can be determined from temperature, humidity, and sunlight intensity (Kamens et al. 1988). Incorporation of decay constants into the PAH source signatures may improve their use as tracers in organic receptor modeling. This report will examine the compositional differences between PAH source profiles from gasoline, diesel and wood combustion and will explore the use of these data to develop a methodology for using PAHs compounds as tracers for source identification.

Literature review

Based on source inventories and meteorological parameters, source oriented dispersion models have been the primary tools for estimating the impact of a particular source at a receptor site. Budiansky (1980) reviewed the

use of dispersion models and showed that when these models are used in assessing source impacts, the error in predicted contributions may vary from 30% to a factor of 2, depending on averaging time, the spatial scales and the terrain. However the major uncertainty is in the source emission rate, according to Van der Horven, chief of the National Oceanic and Atmospheric Administrations Air Resources Environmental Laboratory (Budiansky 1980). Unfortunately, the source term is not often well known to within a factor of 2. Moreover, dispersion models have certain difficulties in predicting short-term impacts and impacts from non-stack sources. Because of the difficulties, the use of receptor oriented models has become more appealing since the 1970's (Cooper and Watson 1980).

Receptor oriented models use source "fingerprints" in receptor samples to assess the contributions from various sources to a sample site (Cooper and Watson 1980). The fingerprint can be either the chemical or physical characteristics of source emissions. In this paper, we will be only concerned about chemical characteristics.

The Chemical Mass Balance method, based on trace element spectra, was proposed first by Miller et al. (1972) and Friedlander (1973). This method has been applied in California (Gartrell and Friedlander 1975), Washington, D.C. (Kowalczyk et al. 1982), and Philadelphia (Dzubay et al. 1988).

Friedlander (1973) classified particulate sources into three types. They were primary natural sources, primary man-made sources, and secondary aerosol formation. Natural sources include soil dust and sea salt. Man-made sources include automobile exhaust, fuel oil, fly ash, cement dust, and industrial emissions. Secondary aerosols are primarily composed of carbon and sulfate plus related ions and water. For example, in a study in Washington, D.C. (Kowalczyk et al. 1982) seven sources were identified with eight marker elements. The predicted contribution from each source is shown in Table 1.

Table 1: Source contributions at Washington, D.C. study

<u>Source</u>	<u>Marker Element</u>	<u>Predicted Contribution</u> (ug/m ³)
coal	Al, As, Fe	5.5
Soil	Al, Fe, Mn	21.4
Refuse	Zn	1.3
Motor vehicle	Pb	8.7
Sea salt	Na	0.9
Oil	V	0.7
Secondary aerosols	SO ₄ , NH ₄ , NO ₃	15.4
Total predicted mass concentration		53.9
Observed TSP		69

Many studies show that automobile emissions play an important role in urban areas. For example, 20-25% of the total suspended particulates (TSP) are contributed by automobile emissions in New York city (Kleinman 1980), and 16% in Washington D.C. (Kowalczyk et al. 1982). Although

only 4-6% of the mass of PM-10 particles (particle diameter smaller than 10 μm) related to vehicle exhaust in Philadelphia (Dzubay et al. 1988), and 8.2% was related to the mass of TSP in Pasadena, California (Friedlander 1973), vehicle exhaust is still a major contributor among man-made sources.

After the oil embargo occurred in 1973, residential wood combustion became popular, and the resulting emissions have become wide spread (Cooper 1980, Quraishi 1985). The first direct determinations of the impact of wood emissions were made by Cooper (1980) in Portland, Oregon with two methods, namely chemical mass balance and C-14 measurements. Each of these two methods independently showed that 51% of the respirable air particulates in January 1978 ($35\mu\text{g}/\text{m}^3$) were from wood smoke in Portland.

The reason to investigate emissions from wood smoke is not only because of the mass of pollutants emitted, but because of the respirable nature and chemical composition of the emissions (Quaraishi 1985). Meyer (1981) reported that approximately 40% of the total polycyclic organic matter, which is the most significant health hazard in residential wood combustion emissions, may be related to residential wood combustion in the United States. Many PAH compounds are suspected human carcinogens.

Although the CMB model has been successfully applied in many areas to identify specific sources, there are a few

limitations in using it with elemental tracers. For example, sources sharing a similar emission pattern, cannot be differentiated. Thus, sources that lack a unique elemental signature will be difficult to distinguish on the basis of elemental data only.

Typical Pb concentrations due to motor vehicle emissions in the United States have declined from 1-2 $\mu\text{g}/\text{m}^3$ in 1972 (Friedlander 1973) to 180 ng/m^3 in 1982 (Dzubay 1988). It has also been a worldwide trend to reduce the lead content of gasoline in order to reduce lead emissions into the atmosphere. The Pb concentration is expected to continue to decline. By 1990 lead containing gasoline became unavailable in many parts of the United States. Therefore, an alternative tracer for identification of motor vehicle emissions is necessary (Gordon 1988, Daisey et al. 1986). Moreover, diesel engines emit particulate matter at a rate 30-100 times higher than does an equivalent sized gasoline powered engine (NRC 1982), but we lack a unique tracer to distinguish diesel from gasoline engines.

As for wood combustion, potassium (K) is the most frequently used tracer (Watson 1979, Gordon 1988). But, it is far from ideal. Gordon (1988) indicated that "it is risky to use total K for wood combustion unless one has extensive knowledge of the many other sources of K, such as lime kilns, soil, and incinerators." Also, K emissions may vary on a large scale, between 530 and 230,000 μg of "K" per

g of particle emitted. It also is not consistent between different kinds of stoves or fireplaces and may change under different operating conditions (Hopke 1985). Sexton et al. (1985) reported that because of the uncertainty of K in wood soot, the CMB approach was not appropriate to estimate the contribution of wood combustion in Waterbury, Vermont project. On the other hand, Lewis et al. (1986) discovered a way to use fine particle corrected potassium concentration (K') in a multiple linear regression (MLR) model and obtained very good wood combustion results in Denver. To obtain a purer tracer variable, the corrected K' was generated by subtracting the K in estimated fine soil contribution from the measured K concentration. The success of this study in Denver was most probably due to a good knowledge of the sources as obtained by factor analysis and the fact that wood smoke and soil were the only important sources of K in Denver. Because inorganic elements can not always provide adequate CMB signatures to identify combustion sources, organic compounds have been considered to be important alternatives (Gordon 1988).

Carbonaceous compounds or organic compounds constitute a major fraction of gaseous and particulate air pollutants. Many gas phase volatile organic compounds (VOC) and particle phase solvent extractable compounds have been characterized in different sources. Scheff et al. (1989) have evaluated 10 sources of VOC and developed source fingerprints. These

sources were categorized into three major groups: (1) vehicles, gasoline vapor and petroleum refineries, (2) solvent sources including architectural coating, print ink and auto painting, and (3) the sources of chlorinated organics, including vapor degreasing, dry-cleaning and waste-water treatment. The fingerprints were presented for a group of 23 compounds, including C2-C6 alkanes, aromatics and chlorinated organics. The conclusion from this study was that the fingerprints have general applicability. Chemical mass balance with VOC fingerprints has been applied for winter-time source-reconciliation of ambient organics in the Chicago metropolitan area (Aronian et al. 1989, O'Shea et al. 1988). The average predictions were generally very consistent with emission inventories. Aronian et al. (1989) concluded that "This study demonstrates that the CMB can be applied to ambient air concentrations of organic compounds and be used to evaluate and validate an area's emission inventory."

Particle phase solvent extractive compounds from combustion particles include hydrocarbons, esters, ketones, PAH, nitro-PAH, oxy-PAH, phenols, organic acids, and so on. Some specific compounds like PAH showed a strong carcinogenic and mutagenic health risk in epidemiological studies and studies on animals (LRE 1978, Bond et al. 1980, Handa et al. 1984). The characterization of these compounds shows that petroleum residues are major and usually

predominant components of the extractable organic compounds from aerosols in urban and suburban areas (Simoneit 1982, 1984). Boone (1987) measured methyl and linear C₂₄-C₃₀ alkanes in ambient and source aerosols, and suggested that alkane isomer composition may provide a valuable tool for distinguishing between emissions from unleaded gasoline fueled and diesel fueled vehicles. Simoneit (1985) indicated that the sterane and 17(H)-hopane distribution signatures are specific for petroleum residues. These compounds can be used for distinguishing vehicular exhaust from the natural background. Hawthorne et al. (1989) indicated that guaiacol derivatives should be the useful tracers for wood smoke pollution regardless of the type of wood burned and syringol derivatives can be used to differentiate the hardwood and softwood burning. 1-methyl-7-isopropylphenanthrene (retene) has also been proposed (Ramdahl 1983) as a unique tracer for wood combustion, but it is also present in other sources like coal emissions.

The compounds mentioned above are characterized to identify specific sources. In addition, PAHs have received most attention because they are generated by all fossil fuel combustion processes (La Flamme et al. 1978, Youngblood et al. 1975). The presence of PAH mixtures in combustion emissions and in smokes from vegetative and fossil fuel materials has been amply demonstrated (Thomas 1968, Lao 1973, Lee 1976). The annual average contribution of PAHs

from a variety of different sources which include the combustion of wood, diesel fuel, gasoline, coke production, etc. is shown in Table 2. As can be seen, residential wood combustion and gasoline vehicles are the two most prominent sources of PAH in the continental USA (Peters et al. 1981).

Daisey et al. (1986) reviewed available data, on particle phase organic compounds in emissions from combustion sources, to determine their potential usefulness in receptor modeling. They pointed out that PAHs, alkanes, and some distinct organic compounds may be useful in distinguishing among emissions from certain particulate pollutant sources. As for PAH, Daisey et al. (1986) indicated two important facts relevant to using PAHs as tracers in receptor modeling. First of all, the PAH profiles of sources which have been repeatedly sampled and analyzed by the same investigator, appear to be fairly reproducible. Secondly, current data indicate that there are compositional differences that can be exploited for source differentiation. Overall, PAHs in particulates appear to be promising for combustion source differentiation because: (1) good sampling and analytical methods already exist for PAHs, and (2) existing PAH data provide a basis for selecting those compounds which are likely to be most stable in the atmosphere.

In particular, the ratios of Benzo[a]pyrene (BaP) to Coronene (Cor), Benzo[ghi]perylene (BgP) to Corenene

Table 2: Estimates of annual PAH emissions by source type
(Peters et al. 1981)

Source type	Estimated annual PAH emissions, metric tons	Percent of PAH total emissions from all sources
Residential heating		
wood-fired total	3,839	34.8
coal-fired	102	0.9
oil-fired	7.4	<0.1
gas-fired	9.8	<0.1
Opening burning sources		
agriculture open burning	1,190	10.8
prescribed burning	1,071	9.7
forest wildfires	1,478	13.4
coal refuse piles	28.5	0.3
land cleaning waste burning	171	1.6
structure fire	86	0.8
Mobile sources		
autos-gasoline	2,160.8	19.6
vehicles-diesel	104.7	0.9
Coke production	632	5.7
Industrial boiler		
coal	69.0	0.6
oil	1.3	<0.1
gas	2.1	<0.1
others	1.5	<0.1
Incinerators		
municipal	0.3	<0.1
commercial	55.8	0.5
Utility boiler		
coal	12.9	0.1
oil	0.3	<0.1
gas	0.3	<0.1
Carbon black	3.1	<0.1
Charcoal manufacturing	1.5	<0.1
Asphalt production	4.3	<0.1
Barium chemical	0.3	<0.1
Total	11,031	

(Mainwaring and Sterling 1981) and BaP to Pb (Freise et al. 1986) have been used to estimate the relative aerosol contributions from automobile exhaust and fossil fuel combustion. Pratsinis (1989) examined these semiquantitative methods that use ratios of PAH compounds and acknowledged that they can be used as an exploratory tool.

Daisey et al. (1979, 1985) applied CMB models to organic species data in order to estimate the BaP source contributions, but the application was not successful due to poor characterization of the PAH source profiles. On the other hand, good agreement between source contributions deduced by CMB and emission inventories was found in a study of fine carbonaceous aerosol at Portland, OR (Shah and Huntzicker 1984). The success of their analysis, as Pratsinis (1989) indicated, was the result of well constructed emission inventories.

Larson et al. (1988) combined trace elements and six PAHs with low volatility in a CMB model to identify sources. A set of 10 day/night sample pairs was collected at Lake Forest Park, WA from January 10, 1988 to January 27, 1988. PAHs in this study included benzo[e]pyrene (BeP), benzo[a]pyrene (BaP), perylene (Pr), indenopyrene (Ind), dibenzoanthracene (DbA) and benzoperylene (BPr), and sources included wood-burning, mobile, road dust, cement, arc furnace and industrial boiler emissions. The predicted mass

concentration was in good agreement with the measured mass concentration.

Miguel and Pereira (1989) pointed out benzo(k)fluoranthene (BkF), benzo(ghi)perylene (BgP) and indeno(1,2,3-cd)pyrene (Ind) can be successfully used as tracers of automotive emissions in receptor sites where there were no other major sources of PAHs. The study was conducted during August, 1984, i.e. the winter time in the southern hemisphere. Based on using CMB model with these three PAH tracers, 21% of TSP was contributed by automotive emissions. This is in good agreement with 24% obtained with elemental carbon and volatilized organic carbon as tracers. These three PAH compounds used in the study show no significant decay occurred during atmospheric transport.

In general, to determine source contributions, the CMB model is quite effective with inorganic species, but has limited success with organic compounds. The major difficulties with the latter are variability of source profile and degradation of these compounds after release into atmosphere (Gordon 1988, Daisey 1986, Pratsinis 1989). Therefore, reliable source profiles and known decay rates of organic compounds are necessary conditions for using the CMB model effectively with PAH.

II. APPROACH

In this paper, the use of reactive compounds as tracers in a CMB model for source contribution identification will be undertaken. PAH compounds were selected as tracers for combustion aerosols. To do this, the following tasks were attempted:

- 1.) A CMB performance testing program was written to evaluate the errors associated with variability in the source signatures, variability in ambient measurements, and variability in source contributions.
- 2.) PAH signatures were characterized from different sources, and differences in PAH patterns between different sources were obtained.
- 3.) Different ways of inputting PAH signatures into the CMB model were explored. This involved using PAH as direct concentrations and as normalized values, to find the optimum way to represent PAH signatures.

4.) The range over which the CMB model produced acceptable solutions was investigated.

5.) A method for introducing PAH decay constants into the CMB model was developed and evaluated with ambient data for which PAH data exist, and receptor modeling has been undertaken using other tracers.

III. CHEMICAL MASS BALANCE (CMB) MODEL

A standard Chemical Mass Balance model, using "effective variance weighted" regression method as recommended by EPA, was used in this paper to compute the relative contributions of different combustion sources to a receptor site (EPA 1988).

Principle

The chemical mass balance method identifies aerosol sources by comparing ambient chemical patterns or fingerprints with source chemical patterns. Conservation of mass between sources and receptors is assumed for both dispersion models and receptor models. In the context of dispersion model, the mass (M_j) that is collected at a receptor site from a given source j is expressed mathematically as the product of atmospheric dispersion factors aggregated together here as D_j , and the mass per unit time that is emitted by a given source, Q_j .

$$M_j = D_j * Q_j$$

From receptor model viewpoint, it is assumed that total mass of a given element or specie like aluminum, sulfate, nitrate, that arrives at a receptor site, is the linear sum of the masses of that individual specie, which arrive at the receptor from each source. Hence we could write an expression for specie i , where m_i is the total mass of specie i measured on a filter sample at a receptor site.

$$m_i = \text{SUM} (F_{ij} * M_j) + e_i \quad j = 1 \text{ to } p$$

where F_{ij} is the fraction of specie i from source j observed in M_j , and e_i is an error term. The number of source types contributing the total mass is equal to p .

Similarly, we could write a mass balance expression which relates the mass concentration of specie i , that is m_i divided by the volume of sampling air, measured on a filter sample at the receptor site to the sum of the contribution of sources:

$$C_i = \text{SUM} (S_j * F_{ij}) + E_i \quad [1]$$

where C_i is the mass concentration of species i in ng/m^3 . S_j is the particulate mass contributed by source j in ug/m^3 (i.e. M_j divided by volume of sampled air) at a receptor site, and E_i represents random error in the measurement of C_i and F_{ij} .

The expanded form of equation [1] for species like aluminum (Al), lead (Pb), and silicon (Si) looks like:

$$C(Al) = (F(Al,1)*S_1)+(F(Al,2)*S_2)+....(F(Al,p)*S_p)+E(Al)$$

$$C(Pb) = (F(Pb,1)*S_1)+(F(Pb,2)*S_2)+....(F(Pb,p)*S_p)+E(Pb)$$

$$C(Si) = (F(Si,1)*S_1)+(F(Si,2)*S_2)+....(F(Si,p)*S_p)+E(Si)$$

Note that the individual mass concentration terms for each source $S_1, S_2, \dots S_p$ are common to each equation and algebraic matrices can be written and manipulated to solve for each of these terms. Two criteria must be met for each specie: (1) The fraction, F_{ij} , for each component and each source (i.e. the source signature) must be known, and 2) all of the major sources must be included.

The least square method is a standard method used to solve a set of linear equations. This calculation produces the most probable values of S_j by minimizing chi-square defined in the expression.

$$\text{chi-square} = \sum (W_i * E_i^2) \quad i = 1 \text{ to } n \quad [2]$$

where E_i has been defined above and W_i is a weighing factor for species i .

The least square solution to equation [1] can be written in matrix form as (Bevington, 1969):

$$S = \text{INV}(F' * W * F) * F' * W * C \quad [3]$$

where W is a diagonal matrix for weighing factors, W_i , F' is the matrix transpose of matrix F, and "INV" denotes matrix inverse.

In the ordinary least square method, only the analytical uncertainty of the ambient concentrations $\sigma(C(i))$ are considered, and the weighing factors are:

$$W_i = \sigma(C_i)^{-2}$$

However, because both $C(i)$ and $F(i,j)$ are averages of measured data, the variations associated with both of these measurements can influence the calculated results. Therefore, the ordinary least square method cannot be expected to provide a reliable solution to equation [1].

Dunker (1979) and Watson (1979) have applied the effective variance least square method to solve the problem. In the effective variance least square method, both the uncertainty of source profile and the uncertainty of sample concentration are included. Since source strengths are unknown, an iterative procedure is followed. Watson et al. (1984) mentioned that the advantages of the effective variance least square method are: (1) the uncertainty of source strengths are calculated, and (2) high precision components give greater influence in the effective variance

least square solution than lower precision ones.

The weighing factor is the reciprocal of the effective variance and is:

$$W_i = [(\sigma(C(i)))^2 + \sum (\sigma(F(i,j)) * S_j)^2]^{-1}$$

where $\sigma(C(i))$ is the uncertainty associated with $C(i)$, and $\sigma(F(i,j))$ is the uncertainty associated with $F(i,j)$

Thus, chi-square for the effective variance method is given by

$$\text{chi-square} = \text{SUM} \frac{E_i^2}{\sigma(C(i))^2 + \sum (\sigma(F(i,j)) * S_j)^2}$$

Limitations of the CMB model

In CMB modeling, there are errors of two types. The first is associated with measurement uncertainties of input data, including source profiles and ambient data, and these are included in the effective variance method as described above. The second type of error are assumptions implicit in the CMB model itself. The basic assumption of CMB model shown in equation [1] is that species should be chemical inert. To reduce errors associated with this assumption, we can select tracer species i that are truly inert or we can modify the model to account for chemical reactions that

affect tracers that are not inert.

In addition to these errors, the limitations of using CMB model are: (1) optimum selection of sources attributed to particulates pollution, (2) representative source profiles for the sources in the area to be modeled, (3) compatible collecting and analyzing systems, and (4) adequate differences between profiles for source identification.

Performance test program

A numerical simulation method was developed for evaluating the performance of CMB model by Javitz et al. (1988). Based on the simulation methodology of Javitz et al., a program was written with the GAUSS mathematical language (for IBM type of personal computers) to test performance of the CMB model with PAH tracers. The program is attached as Appendix A. The processes are described in program flow chart (Figure 1). The input parameters in the program are:

1. The time-averaged contribution of each source at the receptor.
2. The temporal variability in the source contributions. This variability is parameterized as a coefficient of variation (CV), which is an expression of the standard deviation as a percent of mean.

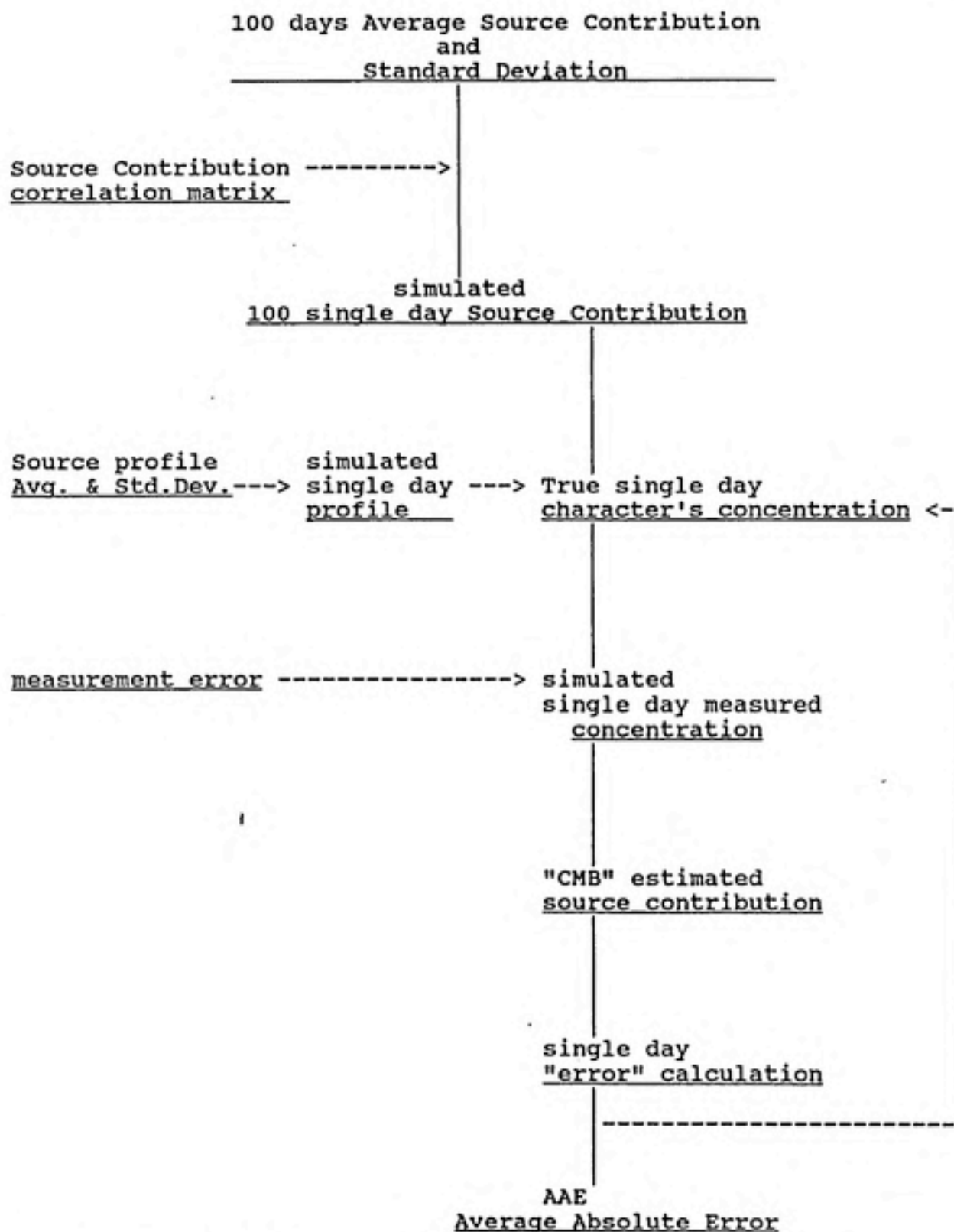


Figure 1. CMB performance testing program flow chart

3. The intercorrelation among the source contributions.
4. The time-averaged source profiles.
5. The temporal variability in the source profiles.
6. The error in species measurement at the receptor.

In the simulations, the parameters are assumed to be lognormally distributed. When parameter X has a mean u and a standard deviation s , the mean and standard deviation for the normal distribution of $\text{LN}(X)$ are derived as follow:

$$\text{Mean}(\text{LN}(x)) = E(\text{LN}(X))$$

$$= E(\text{LN}(u)) + E((X-u)/u) - E((X-u)^2/2u^2) + \dots$$

$$= \text{LN}(u) + 0 - s^2/2u^2 + \dots$$

$$= \text{LN}(u) - 0.5 * \text{LN}(1 + s^2/u^2)$$

$$\text{Var}(\text{LN}(X)) = E(\text{LN}(X) - E(\text{LN}(X)))^2$$

$$= E(\text{LN}(X) - \text{LN}(u) + \dots)^2$$

$$= \text{LN}(1 + s^2/u^2)$$

where $E(\text{LN}(x))$ is the expectancy value of $\text{LN}(x)$. The Taylor's series expansion of $\text{LN}(X)$ is expressed as

$$\text{LN}(X) = \text{LN}(u) + (X-u)/u - (X-u)^2/2u^2 + \dots$$

Thus, the mean and standard deviation of $\text{LN}(X)$ are

$$\text{Mean}(u') = \text{LN}(u) - 0.5 * \text{LN}(1 + \text{CV}'^2)$$

$$\text{standard deviation}(s') = \sqrt{\text{LN}(1 + \text{CV}'^2)}$$

where cv' is the CV value represented as fraction.

In this manner, a Monte Carlo simulation estimates $LN(X)$ with a normal distribution which has a mean of u' and a standard deviation of s' .

Daily source contributions are simulated by mean and CV of time-average source contributions. The daily source profiles for each source are simulated with a mean and CV of average source profiles. The linear addition of the product of the daily source contributions and the daily source profiles are the true daily concentrations of species. The simulated daily concentrations of species are simulated with true daily concentrations of species and measurement errors.

The estimated source contributions are calculated from the CMB model with simulated daily concentrations of fitting species and average source profiles. A measure of the fitting performance is "average absolute error of estimation" (AAE), which is defined as

$$AAE = \text{SUM}(\text{abs}(B_i - T_i)) / n$$

where

n = the number of days of data for the CMB calculation.

($n = 100$ days in this paper)

B_i = the estimated source contribution for a particular i -th day.

T_i = the true source contribution for a particular i -th day.

The program was tested in two parts. First the least square method was tested with a Camden-Philadelphia data set (Dzubay 1988). The results obtained from the Gauss simulation program developed in this study were essentially the same as those reported by Dzubay (1988) as shown in the following table:

Coarse particle component concentrations (ng/m³)

	at site 28 in Camden, NJ					
	soil	marine	incin	vehicle	Sb	SO4
CMB						
program	6721	0	427	599	240	548
(+-)	821	148	148	169	45	426
Gauss						
program	6702	-13	457	593	240	556

In addition, simulations were tested with a simple source combination including geological materials, coal fired power plant, motor vehicle exhaust, and vegetative burning. The Gauss program produced the same results as were obtained by Javitz et al. (1988). Javitz et al. indicated that the source composition variability has the largest effect on the CMB model performance when other sources of error, like receptor measurement variability and correlation among the source contributions, are considered.

IV. DISCUSSION

In this chapter, The uniqueness of PAH profiles for different sources is evaluated and PAH reactivity phenomenon are considered. Then, PAH compounds are used as tracers in CMB model calculations. In the first phase, the PAHs were considered to be inert. In the second phase, PAH reactivity was introduced to improve model predictions.

PAH uniqueness, reactivity & testing in the CMB model

Source profile

PAH Compounds

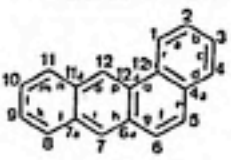
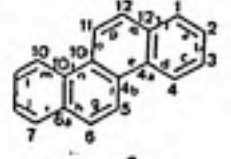

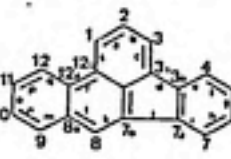
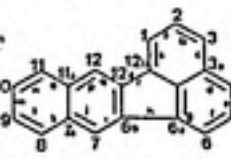
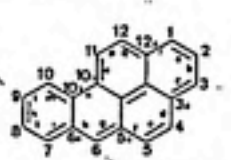
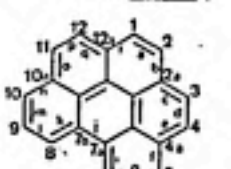
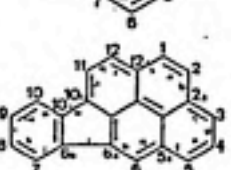
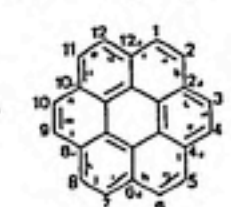
Polycyclic Aromatic Hydrocarbons are considered to be semi-volatile compounds that are distributed in both gas and particle phase. The fraction between the two phases is controlled by the molecular weight of compound, temperature and available adsorption surface on soot particles (Westerholm, 1988, Yamasaki, 1982).

Miguel et al.(1978) reported that detectable amounts of Benzo(a)pyrene (BaP) and Coronene (Cor) were not found in the gas phase, and the majority of BaP and Cor were associated with particles of aerodynamic diameter less than

0.26 μm in a Pasadena, CA aerosol study. Similar conclusions were reached in other studies. From ambient air studies, Yamasaki et al. (1982) stated that "three to five ring PAHs were found in the gas phase depending on temperature, and six ring PAHs were all found in the particulate phase". Westerholm et al. (1988) studied the distribution of PAHs between particles and gas phase from gasoline engine and diesel engine exhaust. He found that the distributions of 2-to 4-ring PAHs between two phase in gasoline engine exhaust were significantly different from that in diesel exhaust. In the case of diesel vehicles, 2-to 4-ring PAHs are adsorbed predominantly on the exhaust particles, but a considerable amount of these compounds are in the gas phase in the case of gasoline vehicles. According to his studies, approximately 30% of Benza(a)anthracene (BaA) (a 4-ring PAH) from gasoline vehicles was found in the gas phase. Vaeck et al. (1984) studied the gas-particle distribution of organic compounds during the four seasons of the year. He found that the particle phase fraction for BaA and Chrysene was 64% in the summer and 91-97% in the other seasons. PAHs of molecular weight 252 and higher were entirely in the particle phase during all four seasons.

PAH data have been collected at the UNC smog chamber facility for a number of years. Nine compounds which are stable in particle phase were selected as potential tracers.

Table 3: PAH compounds selected as potential tracers

<u>compound</u>		<u>mol. wt.</u>	<u>Structure</u>
Benza[a]anthracene	BaA	228	
Chrysene	Chry	228	
Benzo[e]pyrene	BeP	252	
Benzo[b]fluoranthene	BbF	252	
Benzo[k]fluoranthene	BkF	252	
Benzo[a]pyrene	BaP	252	
Benzo[ghi]perylene	BgP	276	
Indeno[1,2,3-cd]pyrene	Ind	276	
Coronene	Cor	300	

These compounds, from Benza[a]anthracene to Coronene, are listed in Table 3.

PAH Emissions from wood combustion & motor vehicles

For each source, the emissions may be varied by the differences in their inherent properties and combustion control. For residential wood combustion (Quraishi 1985), the process of burning is inherently variable and difficult to replicate. Burning rate, heater design, wood loading, type of wood and moisture in the wood may influence the burning emissions. There is also large variability for vehicle emissions (Nikolaou 1984). Fuel composition, air-fuel ratio, driving conditions, vehicle type and vehicle maintenance are important factors.

A number of wood soot studies were conducted in the UNC Teflon smog chamber between 1984 and 1988 (Kamens 1984-1988). The UNC Teflon smog chambers were designed to use natural conditions of light, temperature and humidity to closely simulate outdoor urban atmospheric conditions (Jeffries et al. 1976). Wood smoke from a residential wood stove was added directly to the 25 M³ smog chambers, which initially contained rural background air. Different stoves were used. Ten to 20 minutes after a fire was started, the chambers were charged with fresh soot emissions. The emissions were diluted by 3 to 5 orders of magnitude in the chambers. After adding smoke to the chamber, it was aged

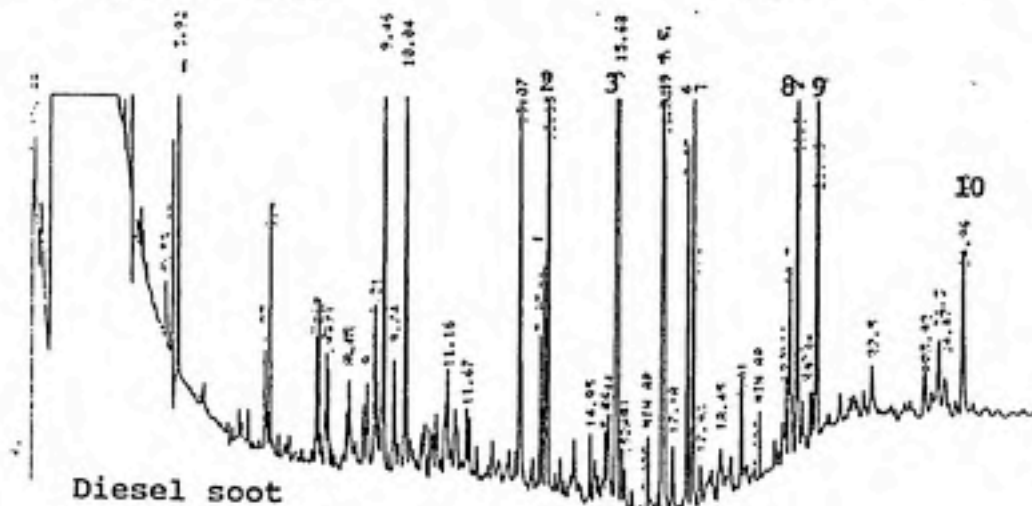
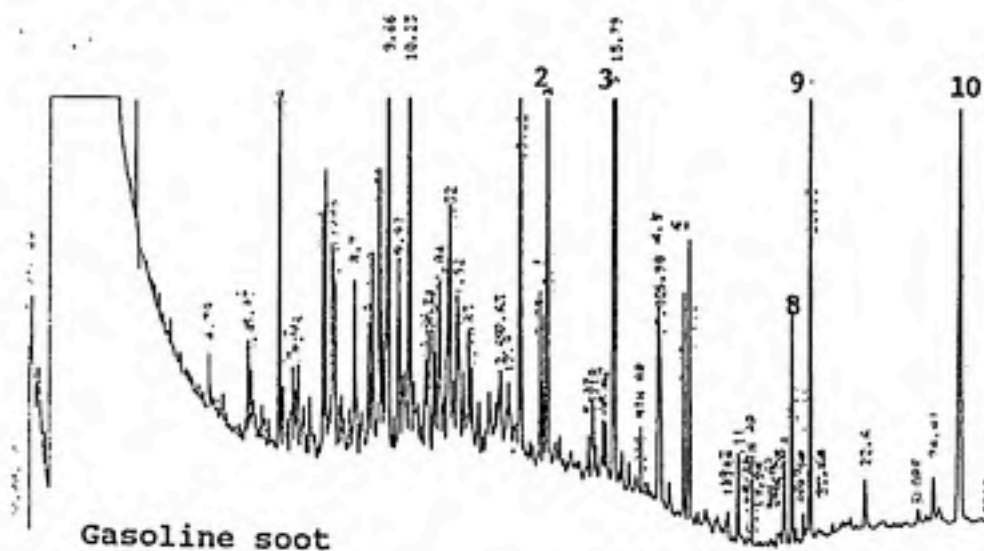
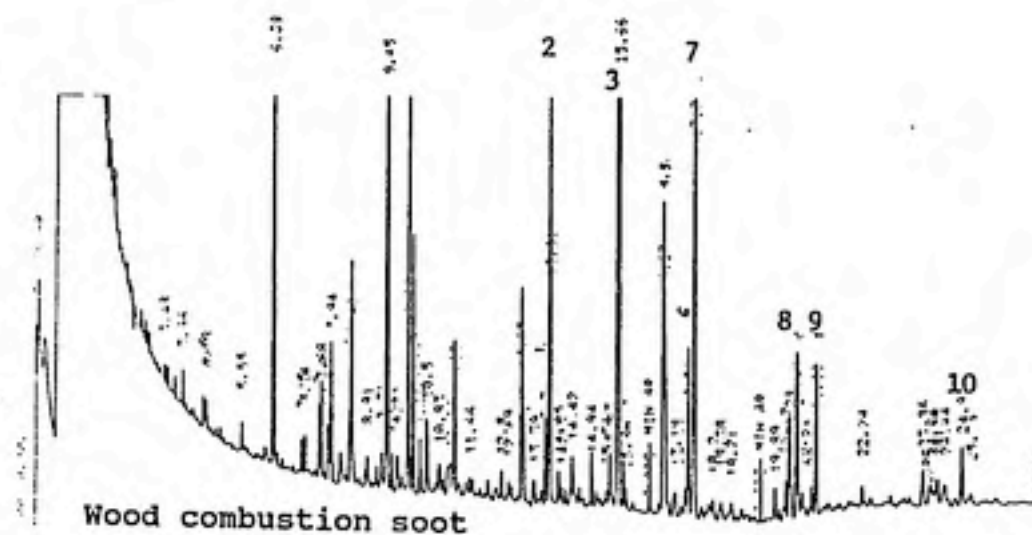
from 2 to 7 hours. Over the aged period, wood soot particle samples were collected on 47-mm Teflon impregnated filters. Filter samples were Soxhlet extracted in the dark with methylene chloride (MeCl_2). PAH concentrations were then analyzed by high performance liquid chromatography (HPLC) with a fluorescent detector and by gas chromatography (GC) with a flame ionization detector. The average source profile for wood stoves from 32 experiments is listed in Table 4. Figure 2 illustrates examples of Gas chromatograms of PAH for wood combustion and gasoline and diesel exhausts.

Compared to wood soot, a smaller number of gasoline engine and diesel engine exhaust experiments were conducted. Table 5 shows the averages and coefficients of variation for gasoline and diesel engine exhausts. Figure 3 shows bar chart plots of the PAH concentrations for three sources.

Table 4: Wood soot PAHs source profile

<u>compound</u>	<u>Concentration</u> (ng/mg)	
	AVG.	C.V. (%)
Benz(a)anthracence	806	94
Chrysene	666	88
Benzo(b)fluoranthene	462	107
Benzo(k)fluoranthene	368	126
Benzo(a)pyrene	515	107
Benzo(e)pyrene	385	99
Benzo(ghi)perylene	321	126
Indeno(1,2,3-cd)pyrene	532	115
Coronene	44	120

* n= 32



Identification of peaks : 1. BaA 2. Chry 3. I.S. 4. BbF
5. BkF 6. BeP 7. BaP 8. Ind 9. BgP 10. Cor

Figure 2: Gas Chromatograms of PAH

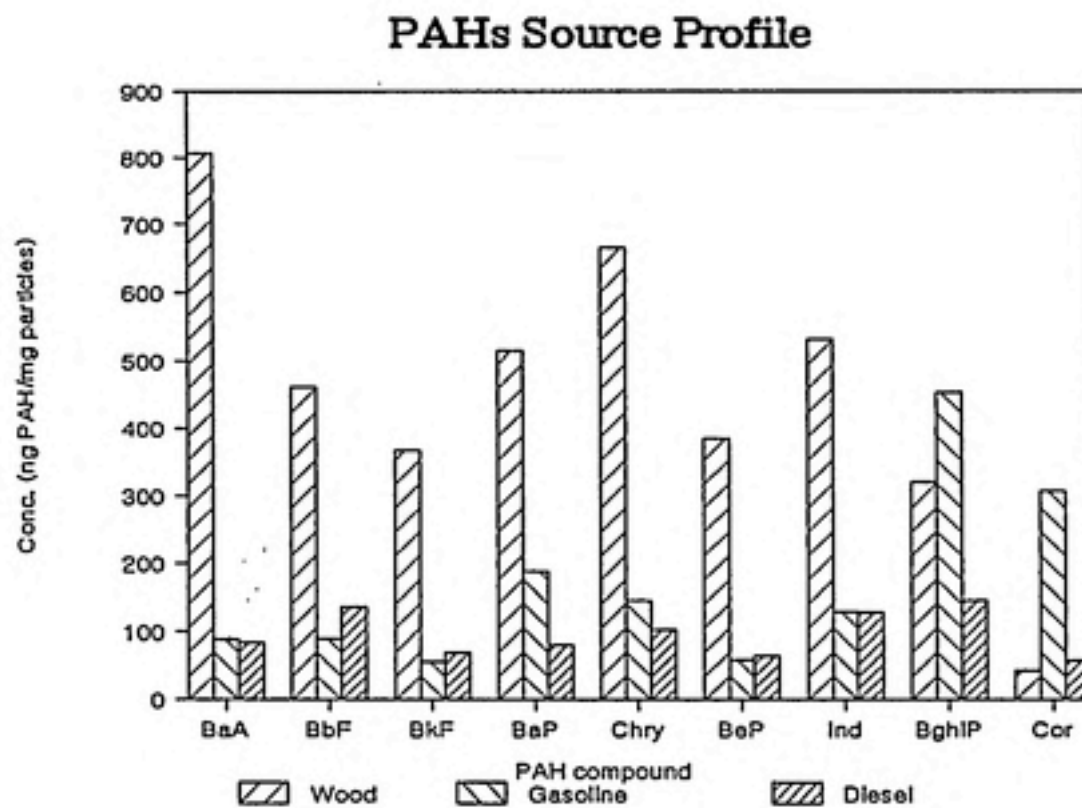


Figure 3: PAH source concentration profiles

Table 5: Gasoline and diesel engine exhausts
PAHs source profile

<u>compound</u>	<u>concentration</u> (ng/mg)			
	<u>gasoline</u>		<u>diesel</u>	
	AVG.	C.V. (%)	AVG.	C.V.
BaA	89	27	85	52
Chry	147	42	103	42
BbF	91	30	166	53
BkF	57	24	70	42
BaP	189	69	81	32
BeP	59	23	65	47
BgP	454	32	147	58
Ind	129	42	128	43
Cor	308	22	58	49
	* n= 5		* n= 3	

However, the emission concentrations of wood combustion obtained from chamber studies can be higher than those from normal residential wood combustion because high PAH loadings were generated purposely in chamber experiments in order to collect particles which contained considerable amount of PAH for analysis. Therefore, the emission concentrations from chamber studies may not be representative of ambient emissions over entire burn cycle. Based on BaP as an indicator, emission concentrations from chamber studies are compared to those from other studies and are shown in Table 6.

Table 6: Comparison of BaP emissions

<u>Resource</u>	<u>BaP emission (ng/mg)</u>
UNC chamber studies	515
Ramdahl (1982)	139
Murphy et al. (1982)	
site 1	100
site 2	137
site 3	83
Knight et al. (1983)	
1	175
2	154

A study by Ramdahl (1982) showed that the BaP emission was 139 ng/mg over a normal wood stove burn cycle of spruce. Ambient BaP and TSP were measured in Telluride, CO by Murphy et al. (1982), where residential wood combustion was the major source of particulate and PAH compounds. Wood contributions at sites were estimated by subtracting the TSP at a background site from the TSP at a site. The BaP emission intensities were then calculated. In addition, Knight et al. (1983) measured the PAH emissions over the full range of wood loads and damper setting for oak cordwood. Table 6 shows that the UNC chamber studies gave BaP to particle ratios 3 to 6 times higher than other studies. Thus, a value of 1/4 of the emission intensity from chamber studies was used to represent the source intensity of residential wood combustion in ambient case studies. For gasoline and diesel emissions, the intensities from chamber studies are used in case studies because a smaller difference (factor of 2) from other studies was shown (Tong 1984, Metz et al 1985).

Uniqueness of PAH signature

In selecting the species to be included in a source signature, one must be concerned with the uniqueness of the tracers in the source. In our example with PAHs, the same PAH compounds may be generated by each source. The utility of using PAHs depends on how different the patterns of the PAHs from each source are. One way to test for this is to determine a parameter called collinearity.

Collinearity is used to denote the situation of one or more collinear relationships among a set of explanatory variables in a linear regression (Belsley et al 1980). In the CMB model, the mass balance equation can not be solved accurately if two or more sources have similar compositional profiles. In order to avoid the linear dependency problem, a single broadly defined source type can sometimes be used to represent a group of similar sources. Since the linear independence between source signatures is essential in the CMB model, collinearity can be used to indicate the adequacy of a source signature.

Each exact linear dependency among columns of the data matrix will produce one zero singular value. Similarly, the presence of near dependencies will result in "small" singular values (or eigen values), according to Kendall (1957) and Silvery (1969). The degree of collinearity depends on how small the ratio of maximum to minimum singular value is. The ratio is defined to be "Condition

index".

The following example from Belsley et al. (1980) illustrates an exact linear dependency. Consider the 6*5 data matrix "X" (Table 7) having the properties that its fifth column is exactly twice its fourth, and both of these are in turn orthogonal to the first three columns.

Table 7: Data matrix for linear dependency example

	-74	80	18	-56	-112
	14	-69	21	52	104
X[6,5] =	66	-72	-5	764	1528
	-12	66	-30	4096	8192
	3	8	-7	-13276	-26552
	4	-12	4	8421	16842

Singular values, obtained by a singular value decomposition (SVD) calculation, are $u_1=170.7$, $u_2=60.5$, $u_3=7.6$, $u_4=36368$, and $u_5=1.3 \times 10^{-12}$. For this data matrix, the condition index is $u_4/u_5= 3 \times 10^{16}$, which is essentially infinite. Singular value judgement shows that exact dependency exists between columns 4 and 5.

Variance-decomposition proportions (Table 8) show that u_5 completely dominates two variances; i.e. the component associated with u_5 accounts for virtually all the variance of both b_4 and b_5 . At the same time, u_3 accounts for 97% or more of $\text{var}(b_1)$, $\text{var}(b_2)$, and $\text{var}(b_3)$. This suggests the presence of a second near dependency in X.

Table 8: Variance-decomposition proportions

Singular Values	Proportions of				
	var(b1)	var(b2)	var(b3)	var(b4)	var(b5)
u1	0.002	0.009	0.000	0.000	0.000
u2	0.019	0.015	0.013	0.000	0.000
u3	0.976	0.972	0.983	0.000	0.000
u4	0.000	0.000	0.000	0.000	0.000
u5	0.003	0.005	0.003	1.000	1.000

Two unfortunate effects occur when collinear source profiles are used. First from a computational point of view, the least square regression will be unstable; i.e. any small change in the elements of the profile matrix will result a large change in the regression results. Second from a statistical perspective, collinear source profiles will decrease the precision of the calculation and the variance will be high.

Generally, weak dependencies are associated with condition indices of around 5 to 10, whereas moderate to strong dependencies are associated with condition indices of 30 to 100 (Belsley et al. 1980).

In this work, the relationships between condition index and CMB model errors were evaluated with simulated data. Two sources, original source and simulated source, were used for condition index test. Based on an original profile, several of different profiles were generated via simulation. Condition indices from 100 profile sets were calculated. Fixing the same source contribution for each source and

using a 10% measurement error for each species, the error of the CMB model results were examined separately with 25% and 50% source profiles variations. This is illustrated in the following example.

A 5-PAH source signature of vehicle emission consisting of BaP, BbF, BkF, BgP, and Ind was used as the original hypothetical profile. One hundred simulated profiles were generated from the original matrix by multiplying each PAH concentration with random numbers between 0 and 5 uniformly. The results show that the AAE of the original profile had a linear relation with condition indices. Linear correlation coefficients are 0.78 for 25% source profile variation, and 0.80 for 50% variation. Figures 4 and 5 show the linear relationships. If we assume that the acceptable average error is $\pm 50\%$ related to average source contribution, the condition index should be less than 13.8 for 25% source profile variation coefficient, and less than 7 for 50%. These results suggest that condition index can be a useful indicator for predicting the compositional difference between profiles.

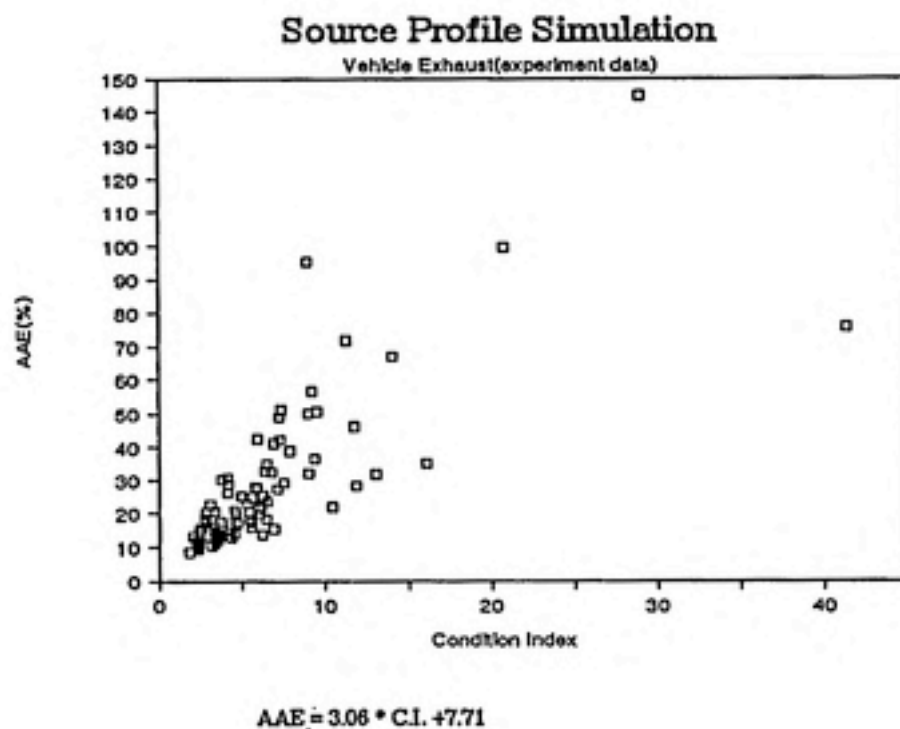


Figure 4: C.I. vs. AAE at 25% source profile variation

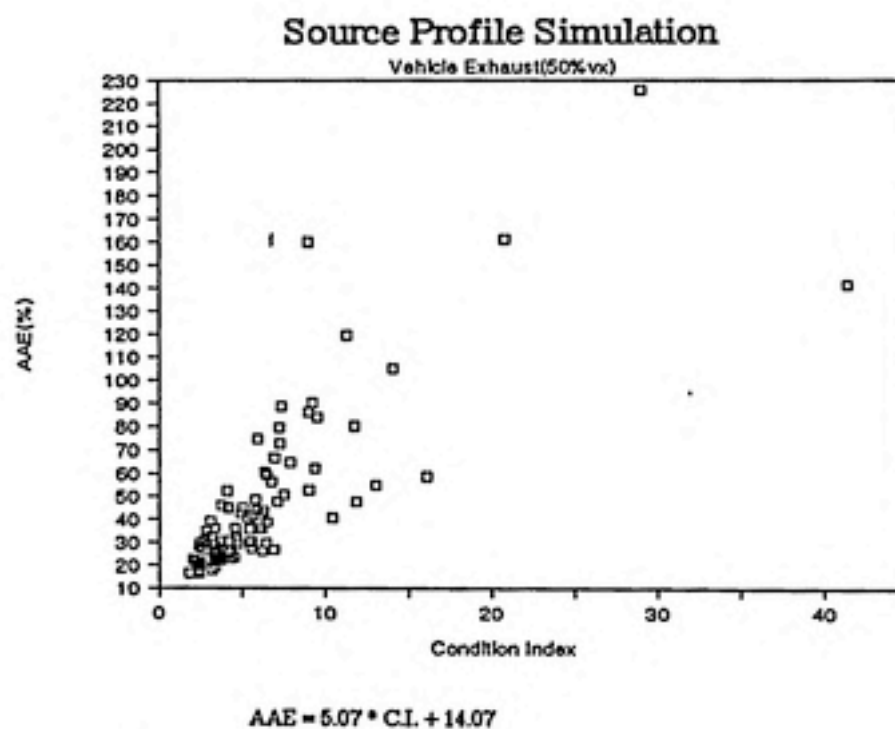


Figure 5: C.I. vs. AAE at 50% source profile variation

Reactivity

One feature of the CMB model represented by equation [1] is that the tracer compounds are chemically conserved, and the source signatures do not change between source and receptor. However, if selected tracer compounds react during transport between the source and receptor, a change in the source pattern will occur and the validity of the signature for use in equation [1] will be lost. Butler and Crossley (1981) studied the role of metals in dispersion and reaction of PAH compounds in the atmosphere. In their study, fractionated urban aerosols were analyzed with Scanning Electric Microscopy. Their results showed that the PAH content of aerosol particles belongs uniquely to the sub-micron size fraction, in which the crustal elements Al and Si and the transition metal Fe, Cu and Zn are absent. This study strongly suggests that these metals do not act as carriers of PAHs during their dispersion in the atmosphere or act as catalysts for promoting reaction. Light, temperature, oxidants in the air as well as the substrate on which PAH are adsorbed, are the predominant factors which influence the rate of degradation (Nikolaou 1984, Behymer 1988). The loss of PAH on fly ash substrate (Behymer 1988) and combustion soot particles (Kamens et al. 1988) may be approximated as first order process.

Many researchers have investigated PAH degradation with respect to different parameters. Miguel (1984) studied PAH

decay on tunnel particles by exposing PAHs to ambient air (without exposure to direct sunlight) for up to 100 hours, and calculated half-lives for several PAH compounds.

Grosjean et al. (1983) conducted an experiment in which PAHs were exposed in the dark to pure humid air, 100 ppb of ozone, 100 ppb of SO₂, 100 ppb of nitric acid free NO₂, and particle free ambient air. The PAHs were deposited on different substrate, including fly ash, diesel exhaust and ambient particles. In their study no reaction was observed after 3 hours of exposure. Behymer and Hites (1988) pointed out that PAH photolytic processes are independent of PAH structure but are dependent on the physical and chemical nature of the substrate. Their experiments were conducted with PAH deposited on 15 kinds of coal fly ash samples. These PAHs were also exposed to a mercury vapor lamp light source with a measured irradiance of $17.6 \pm 1.4 \text{ W/m}^2$.

Butler and Crossley (1981) examined the degradation of PAH adsorbed on soot particles by exposing them to air containing 10 ppm NO_x for periods of up to 50 days. In their study, they found that nitration can be an effective route for the removal of PAHs from the atmosphere. Table 9 lists half-life of PAHs estimated in the three studies mentioned above.

Table 9: Half-life of PAHs in hours

Compound	Miguel (1984)	Behymer et al. (1988)	Butler et al. (1981)
BaA		19 - 1000	264
Chry	36	152 - 1000	648
BbF			
BkF	53		
BaP	29	28 - 1000	168
BeP		163 - 1000	576
Ind	50	120 - 1000	
BgP	48	119 - 1000	192
Cor	360	115 - 1000	696

Kamens and co-workers (1988) quantified the loss of PAH on atmospheric soot particles with respect to the effects of humidity, solar radiation, and temperature. It was suggested that "ambient water vapor and light intensity can be used as the two most important predictors of the rate constants". Table 10 shows an example of using specific light intensity and humidity to estimate half life of PAH compounds.

The empirical relationship in the Kamens et al. study (1988) was derived from wood soot PAH degradation studies. Since there is a limited data base for gasoline and diesel exhausts, the same decay rate as wood soot will be used. Support for this idea comes from a parallel chamber experiment with wood combustion and gasoline engine exhaust conducted on April 5, 1985. Both soot systems were aged in the chamber under sunlight and evening conditions. Measured data on the decay of PAH concentrations are shown in Figure

6. The first order decay constants were calculated and are listed in Table 11. It shows similar degradation for the two different sources.

Table 10: Estimated PAH half-life (Kamens et al. 1988)

	<u>HALF - LIFE (hours)</u>		
	light*=1 10g/m ³ H ₂ O	light=0.8 4g/m ³ H ₂ O	light=0.4 2g/m ³ H ₂ O
BaA	0.4	2.2	7
Chry	1.3	7.7	25
BbF	1.3	3.7	10
BkF	0.8	3.2	11
BaP	0.5	2.1	6
Ind	0.8	8.8	39
BgP	0.6	3.1	12

* light intensity = cal/cm².min.

Table 11: Decay constants for parallel experiment (Kamens 1984-1988)

	<u>Decay Constant</u>	
	(min ⁻¹)	
	Gasoline	Wood
BaA	0.00783	0.00685
Chry	0.00384	0.00261
BbF	0.00212	0.00263
BkF	0.00307	0.00369
BaP	0.00726	0.00701
Ind	0.00336	0.00376
BgP	0.00423	0.00472
BeP	---	0.00224
Cor	0.00168	---

Decay of PAH on Parallel Experiment

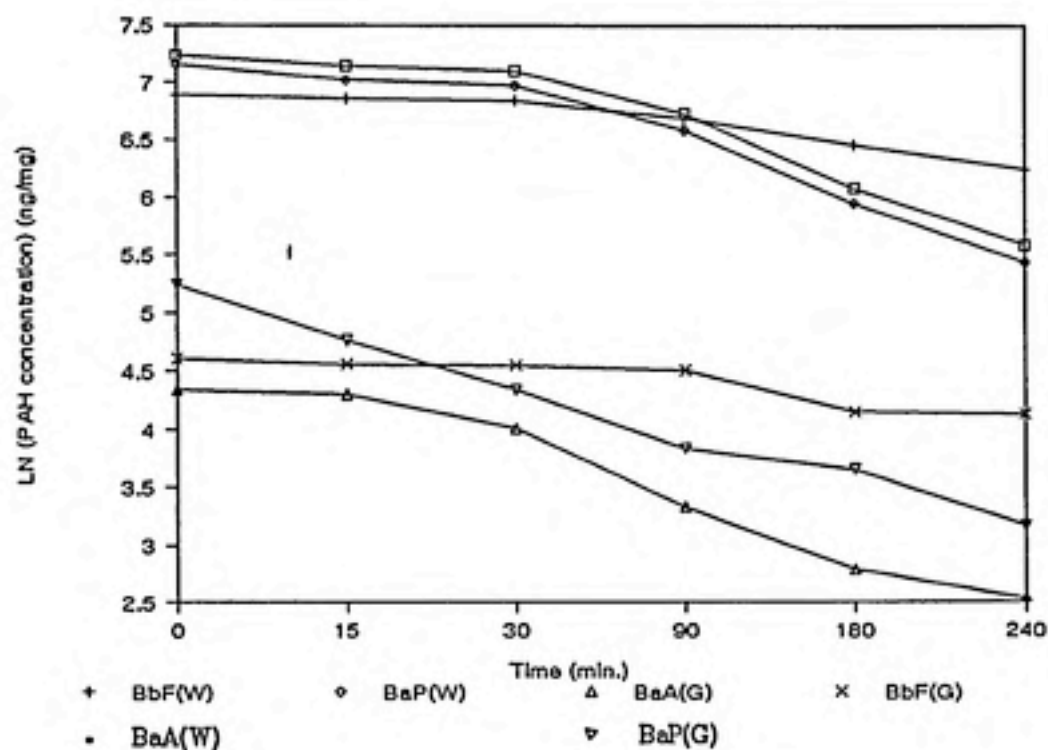
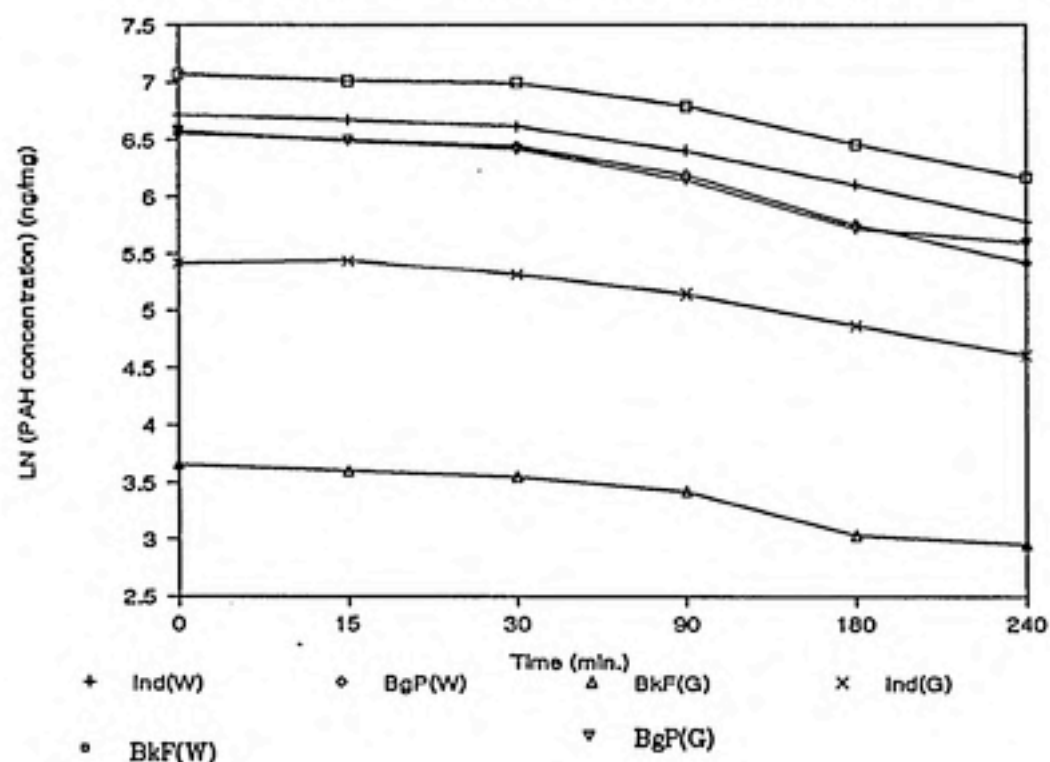


Figure 6: Decay of PAH on parallel experiment

Source signature

PAH source signatures for different combustion sources are developed in this section. Combustion source emissions are known to have an inherent high variation. However, many studies pointed out that some specific PAH or ratios between PAH compounds may be used for source identification. Greenberg et al. (1981) indicated that Coronene (Cor) and Benzo[ghi]perylene (BgP) may be good indicators of automobile traffic. Cretney et al. (1985) suggested that the ratio of Benzofluoranthrenes (BF) to Benzo[ghi]perylene (BgP) can be used to distinguish between domestic fires and automobiles. Hering et al. (1984) suggested that the ratios of BbF and BkF to carbon monoxide (BbF/CO and BkF/CO) may provide tracers for diesel engine identification.

All these findings suggest that concentration ratios may be used as source signature. Based on the UNC PAH data base, ratios between different PAHs were calculated, and the average and variation of these ratios for three sources are shown in Table 12. Some ratios in the wood combustion source, such as BaA/BaP, Ind/BgP, have a much lower variation than concentration strength from the sources. This means that the concentration relationship between these compounds might be independent of different operating conditions.

Conceptionally, if two compounds have the same reactivity, the relative concentration in a source profile

will remain constant over the transport process. Because of this property, the ratios were examined, with special emphasis on those for compounds with similar reactivity.

Although the half-life of PAH from different studies, shown in Table 9 and 10, are not consistent, the relative reactivities are more similar. Table 10 shows that the reactivity of BaA and BaP are similar at three conditions, the reactivity of BkF and BgP are also similar at three conditions, but Ind is similar with BgP and BkF at only one condition. Miguel (1984) indicated that the reactivity of BgP, Ind and BkF are similar from his tunnel particle study.

Miguel (1989) observed that the ratios of BaA to BaP, BghiP to Ind and BkF to Ind have similar values for both tunnel and ambient conditions. In a study of PAH degradation on 15 kinds of fly ash substrate, Behymer (1988) used a "t" test to show that the reactivities of Cor. vs. BgP, BaA vs. BaP, and BeP vs. Chry are similar in almost all cases. According to these studies, ratios between similarly reactive compounds may be useful as source signatures. Table 13 shows a comparison of ratio data from UNC chamber experiments to those from other studies. The comparison shows that some of these ratios, such as BgP/Cor, BgP/Ind and Chry/BeP, are consistent, but the BaA/BaP ratio differs significantly among the various studies.

Based on the UNC data shown in Table 13, Figure 7 illustrates the ratios from diesel, gasoline and wood soot

in bar chart form. Gasoline exhaust has a lower BgP/Cor value (1.46) than the wood combustion ratio (3.42). In contrast, gasoline exhaust has higher BgP/Ind ratio (3.57) than wood combustion ratio (0.8). This is consistent with the conclusion of Greeberg (1981) that Cor and BgP are good indicators of vehicle emissions. Meanwhile, the BbF/Cor ratio is high in wood combustion (3.5) and is low in gasoline exhaust (0.28). This means that the BgP concentration is approximately 5 times that of BbF in gasoline exhaust, but is roughly equal to that in wood combustion. The same ratios for diesel exhaust are somewhere inbetween those for gasoline and wood soot, and may not show enough unique character from wood combustion. An exception may be the Ind/Cor ratio which is 2.1 in diesel exhaust and 4.3 in wood combustion. The above information suggests that PAH compounds may have some characteristics that could enable specific sources to be identified. The following two groups were selected for tracer testing: (1) an Ind group with BbF, Ind, BgP, and Cor, and (2) a BaA group with BaA, BbF, BgP, and Cor. The ratio matrix for these two groups are shown in Table 14 and 15.

Table 12.1: 9-compound ratio matrix for wood combustion

Ratio Matrix (Wood Combustion Emissions)									
	BaA	BbF	BkF	BaP	Chry	BeP	Ind	BgP	Cor
BaA	1.00								
BbF	1.23 (28%)	1.00							
BkF	1.38 (37%)	1.64 (49%)	1.00						
BaP	1.13 (16%)	1.04 (50%)	0.74 (46%)	1.00					
Chry	0.93 (15%)	0.88 (23%)	0.73 (16%)	0.84 (15%)	1.00				
BeP	2.17 (50%)	1.30 (8%)	1.58 (43%)	1.86 (37%)	2.28 (43%)	1.00			
Ind	1.61 (27%)	1.16 (38%)	1.34 (36%)	1.48 (23%)	2.07 (21%)	1.02 (31%)	1.00		
BgP	1.93 (30%)	1.51 (35%)	1.27 (56%)	1.72 (31%)	2.37 (39%)	1.12 (30%)	1.25 (16%)	1.00	
Cor	—	3.50 (10%)	3.06 (8%)	6.72 (7%)	—	—	—	3.42 (6%)	1.00

Table 12.2: 9-compound ratio matrix for gasoline vehicle exhaust

Ratio Matrix (Gasoline engine Exhaust)									
	BaA	BbF	BkF	BaP	Chry	BeP	Ind	BgP	Cor
BaA	1.00								
BbF	1.00 (21%)	1.00							
BkF	1.56 (23%)	1.66 (36%)	1.00						
BaP	0.75 (75%)	0.56 (71%)	0.34 (66%)	1.00					
Chry	0.64 (18%)	0.67 (29%)	0.43 (31%)	1.70 (43%)	1.00				
BeP	1.51 (15%)	1.43 (17%)	1.08 (8%)	4.00 (49%)	2.61 (22%)	1.00			
Ind	0.84 (54%)	0.65 (39%)	0.43 (37%)	1.48 (62%)	1.11 (52%)	0.49 (21%)	1.00		
BgP	0.22 (40%)	0.19 (32%)	0.13 (36%)	0.45 (79%)	0.33 (51%)	0.14 (19%)	0.28 (22%)	1.00	
Cor	0.30 (35%)	0.28 (25%)	0.18 (30%)	0.65 (75%)	0.46 (45%)	0.20 (20%)	0.41 (30%)	1.46 (15%)	1.00

Table 12.3: 9-compound ratio matrix for diesel vehicle exhaust

Ratio Matrix (Diesel Engine Exhaust)									
	BaA	BbF	BkF	BaP	Chry	BeP	Ind	BgP	Cor
BaA	1.00								
BbF	0.47 (24%)*	1.00							
BkF	1.22 (22%)	2.30 (5%)	1.00						
BaP	0.83 (12%)	1.71 (17%)	0.83 (18%)	1.00					
Chry	0.91 (57%)	1.18 (8%)	0.70 (38%)	0.82 (21%)	1.00				
BeP	1.40 (26%)	2.70 (9%)	1.14 (13%)	1.45 (31%)	1.88 (38%)	1.00			
Ind	0.88 (74%)	0.89 (1%)	0.65 (57%)	0.74 (41%)	0.87 (19%)	0.59 (62%)	1.00		
BgP	0.62 (45%)	0.91 (2%)	0.48 (25%)	0.58 (14%)	0.72 (12%)	0.43 (31%)	0.87 (25%)	1.00	
Cor	1.06 (18%)	2.27 (6%)	0.99 (1%)	1.35 (11%)	1.93 (3%)	0.85 (15%)	2.55 (6%)	2.49 (5%)	1.00

Table 13: Ratios of PAH observed in different studies

*** Data Comparison ***

Gasoline Exhaust

	UNC	Grimmer (1977)	Grimmer (1977)	Grimmer (1977)	Stenberg (1983)
BgP/Cor	1.46	1.22	1.07	1.41	2.33
BgP/Ind	3.57	3.73	3.44	4.43	3.5
BkF/Ind	0.43	0.2	0.22	0.4	---
Chry/BeP	2.61	2.1	2.3	---	1.2
BaA/BaP	0.75	1	1	0.2	3.67
BbF/Cor	0.28	0.17	0.17	---	---

Diesel Exhaust

	UNC	H.Y.Tong (1984)			NBS SRM 1650	Willey (1984)
		1.	2.	3.		
BgP/Cor	2.49	2.02	1.47	2.15	---	---
BgP/Ind	1.15	1.06	1.12	1.19	1.04	1.22
BkF/Ind	0.65	0.29	0.41	0.16	0.91	0.45
Chry/BeP	1.88	1.62	1.29	1.79	2.29	---
BaA/BaP	0.83	1.93	1.71	2.38	5.42	0.86
BbF/Cor	2.27	2.11	1.4	1.93	---	---

Wood Combustion

	UNC	Sexton (1985)	Ramdahl (1982)
BgP/Cor	3.42	4.33	---
BgP/Ind	0.8	0.92	1.1
BkF/Ind	1.34	---	---
Chry/BeP	2.28	2.17	2.35
BaA/BaP	1.13	1.5	1.2
BbF/Cor	3.5	---	---

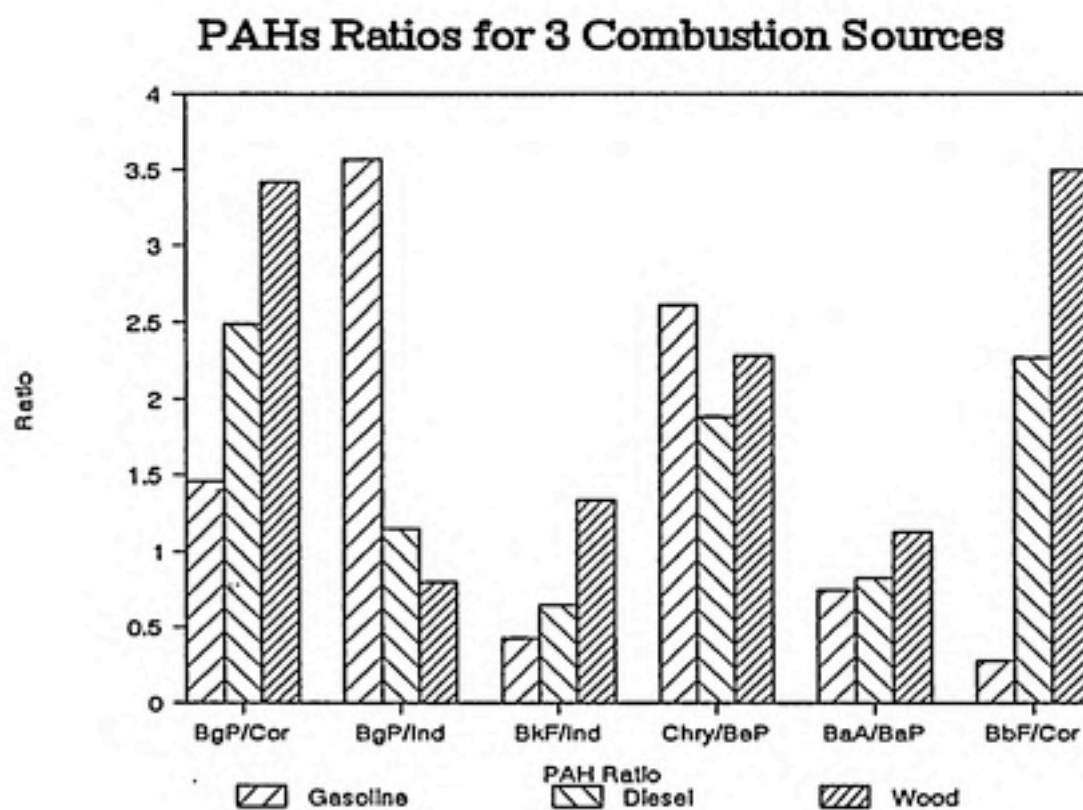


Figure 7: Ratios of PAH observed in three sources

Table 14: Ratio matrix of Ind group

Ratio Matrix (Diesel Engine Exhaust)

	BbF	Ind	BgP	Cor
BbF	1.00			
Ind	0.89 (1%)	1.00		
BgP	0.91 (2%)	0.87 (25%)	1.00	
Cor	2.27 (6%)	2.55 (6%)	2.49 (5%)	1.00

Ratio Matrix (Gasoline engine Exhaust)

	BbF	Ind	BgP	Cor
BbF	1.00			
Ind	0.65 (39%)	1.00		
BgP	0.19 (32%)	0.28 (22%)	1.00	
Cor	0.28 (25%)	0.41 (30%)	1.46 (15%)	1.00

Ratio Matrix (Wood Combustion Emissions)

	BbF	Ind	BgP	Cor
BbF	1.00			
Ind	1.16 (38%)	1.00		
BgP	1.51 (35%)	1.25 (16%)	1.00	
Cor	3.50	—	3.42	1.00

Table 15: Ratio matrix of BaA group

Ratio Matrix (Diesel Engine Exhaust)

	BaA	BbF	BgP	Cor
BaA	1.00			
BbF	0.47 (24%)*	1.00		
BgP	0.62 (45%)	0.91 (2%)	1.00	
Cor	1.06 (18%)	2.27 (6%)	2.49 (5%)	1.00

* Mean (variance%)

Ratio Matrix (Gasoline engine Exhaust)

	BaA	BbF	BgP	Cor
BaA	1.00			
BbF	1.00 (21%)	1.00		
BgP	0.22 (40%)	0.19 (32%)	1.00	
Cor	0.30 (35%)	0.28 (25%)	1.46 (15%)	1.00

Ratio Matrix (Wood Combustion Emissions)

	BaA	BbF	BgP	Cor
BaA	1.00			
BbF	1.23 (28%)	1.00		
BgP	1.93 (30%)	1.51 (35%)	1.00	
Cor	—	3.50 (10%)	3.42 (6%)	1.00

CMB modeling assuming inert PAHs

Concentration method

Most applications of the CMB model use a concentration method with elemental tracers. The tracers are entered into the model as a mass of tracer per mass of particle emitted from the source. In the case that will be discussed here three combustion sources and nine PAH compounds were included. Source concentration profiles for wood, gasoline and diesel source are listed in Tables 4 and 5 of the previous section. These three sources and all the possible combinations of any two sources were tested. From source pattern identification, a nine-compound group and two sets of 4 compounds groups, namely BaA group with BaA/BbF/BgP/Cor and Ind group with BbF/Ind/BgP/Cor, were used. The similarity of the source profiles were evaluated, based on the calculation of condition index (C.I.). Table 16 shows that C.I. values of wood/gasoline/diesel (W/G/D) and wood/diesel (W/D) combinations are larger than those of W/G or G/D combination. As it was mentioned previously, when the C.I. value is greater than 13.8 for a 50% uncertainty, it is difficult to conclude that the two sources are very different. One would therefore predict that wood combustion and diesel engine exhaust may be difficult to separate with this method. The condition indices for W/G and G/D combinations with both 9 compound and 4 compound groups are

in a reasonable range. For W/D and W/G/D, the Ind group has a much higher condition index than the BaA group and the 9 compound group. The condition indices of BaA group are similar to those of 9 compound group for all combinations. Although the concentration method can solve the W/G and G/D, more PAH fitting species would be necessary to better resolve the W/G/D or W/D source combinations (see Table 16).

Table 16: Condition Index for concentration method

<u>Source combination</u>	<u>Condition Index</u>		
	<u>9 compound group</u>	<u>Ind group</u>	<u>BaA group</u>
W / G / D	20.0	206.0	27.0
W / G	3.2	3.5	3.2
W / D	12.0	31.0	15.0
G / D	4.5	4.5	5.0

* Ind group : BbF, Ind, BgP, Cor.
 BaA group : BaA, BbF, BgP, Cor.
 W : wood combustion source
 G : gasoline-engine exhaust
 D : diesel-engine exhaust

With the assumption that a maximum acceptable error in model estimation is 50%, the acceptable conditions under which the model will work were tested for each source combination. A 10% measurement error was assumed when we tested the absolute average error with different source strength ratios. The test data are listed in Table 17 and the acceptable ranges are shown in Figure 8. The test data

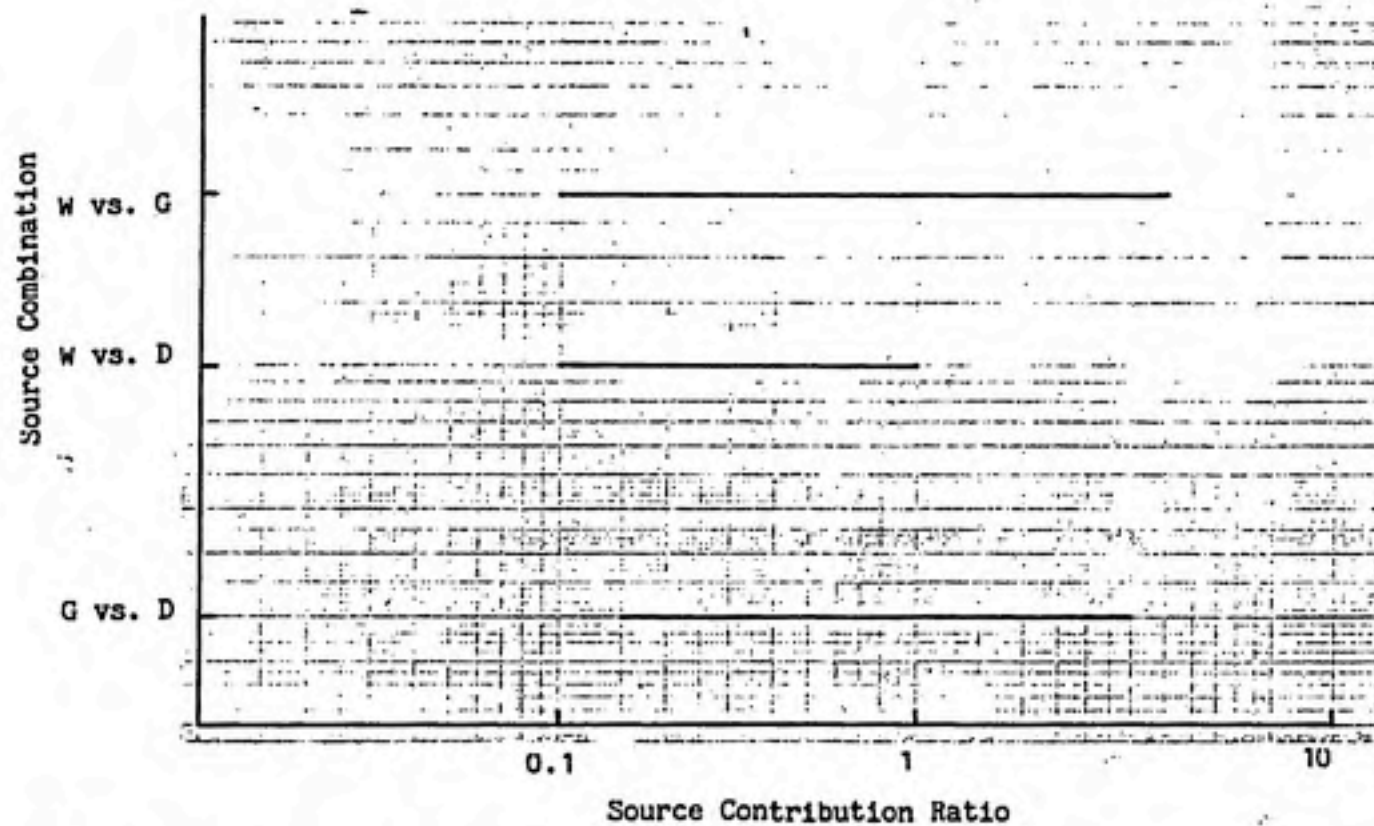


Figure 8 : Acceptable Range for Concentration Method

Table 17: Acceptable condition test
with
9 compounds concentration

Contribution Ratio			AAE (%)		
W	G	D	W	G	D
1	1	1	35	31	128
1	0.5	1	36	43	110
1	0.1	1	36	134	82
0.5	1	1	35	29	91
0.1	1	1	80	24	51
1	1	0.5	38	28	220
10	1		24	81	
5	1		16	49	
2	1		15	28	
1	1		13	22	
1	2		18	18	
1	5		29	17	
1	10		43	16	
1		1	27		58
1		2	29		43
1		5	40		33
1		10	56		30
	10	1		12	114
	5	1		12	65
	2	1		12	35
	1	1		14	26
	1	2		20	22
	1	5		36	25
	1	10		61	25

show that the concentration method performed poorly when three sources were used. For any combination of two sources, the acceptable conditions, expressed as a source contribution ratio, are between 1 and 0.1 for wood and diesel sources (W/D ratio), between 4 and 0.15 for gasoline and diesel source (G/D ratio), and between 5 and 0.1 for wood and gasoline source (W/G ratio). In the concentration method, large concentration differences decrease the ability of source identification. For example, wood combustion generally emits much higher PAHs than diesel engine per unit particle mass. Thus, the source concentration of diesel exhaust may be within the variation of wood combustion. This makes it difficult to identify diesel in the presence of large wood smoke emissions.

The advantages of concentration method are (1) it is easy to combine with other non-PAH tracers, like potassium etc., and (2) It can be used to estimate source contribution directly. The disadvantages, however, are (1) high source strength variations introduce large errors, this is especially true for wood combustion sources, and (2) a limited acceptable range due to profile similarity.

Normalized concentration method

The stable ratios between PAHs, illustrated in Table 10, suggest that a stable source pattern exists in terms of normalized concentration. This requires that a source

emission equals the basic source pattern times an intensity factor. For example, Figure 9 shows four different wood soot samples taken from the UNC chambers at different times for the BaA group. A generalized normalized group is also shown. A similar pattern in concentration profiles suggests that any single source emission can be represented as a stable pattern with a different intensity due to a different emission intensity.

The advantage of the normalized concentration method is that the method focuses predominantly on source pattern character and eliminates the influence of the source intensity (i.e. variability). This means that the ratios among PAHs from given sources remains the same even when the actual emission strength can vary by orders of magnitude.

The normalized concentration $NF(i,j)$ of a fitting compound i for source j is defined in this study as the ratio of the concentration of a fitting compound i to the sum of concentrations of all fitting compounds.

$$NF(i,j) = F(i,j) / R(j)$$

where

$$R(j) = \sum F(i,j) \quad i = 1 \text{ to } n \quad [4]$$

$F(i,j)$ is the concentration of component i in source j emission. The total number of fitting compounds is n .

For BaP at a given receptor from diesel exhaust, the

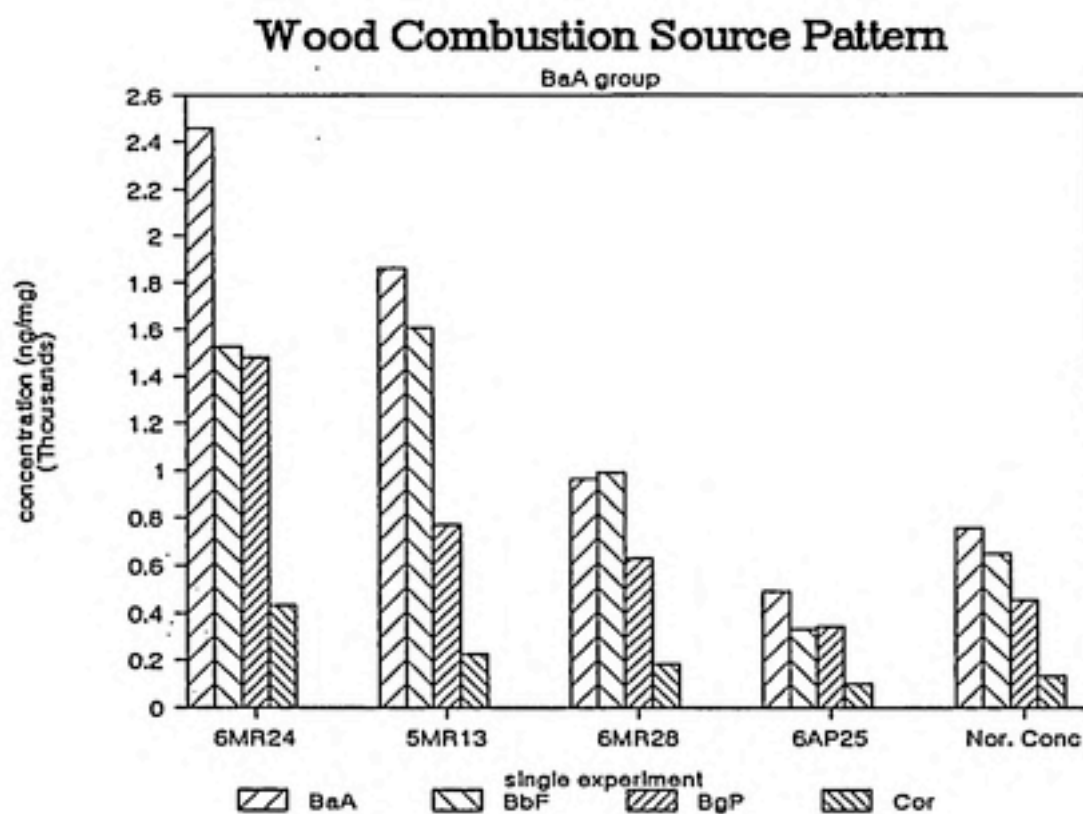


Figure 9: Typical measured profiles and normalized profile for residential wood combustion

equation becomes

$$NF(BaP,D) = \frac{F(BaP,D)}{R(D)}$$

where

$$R(D) = F(BaP,D) + F(BaA,D) + F(BeP,D) + F(Chry,D) + \text{etc.}$$

The mass balance equation [1] with $R(j)$ can be expressed as:

$$C(i) = \text{SUM}(S(j) * R(j) * F(i,j) / R(j))$$

This equation will equal to

$$C(i) = \text{SUM} (S'(j) * NF(i,j)) \quad [5]$$

where $C(i)$, $F(i,j)$, $S(j)$ have the same meaning as the parameters used in equation [1]. $S'(j)$ is the mass of PAH contributed by source j (ng/m^3).

In the normalized concentration method, the weighing factor in effective variance least square method will be

$$W_i = [(\text{sigma}(C(i)))^2 + \text{SUM}(\text{sigma}(NF(i,j) * S'(j))^2)]^{-1}$$

Notice that the interpretation of estimated contributions from normalized concentration method $S'(j)$ are different from those from concentration method $S(j)$, since different forms of input source signatures are used. The estimated contributions from normalized signature represent

the PAH contribution from a given source (mass of PAHs contributed by a source) instead of the particulate source contribution which is calculated from the concentration method. Tables 18, 19, and 20 list the following data: the normalized concentration for the 9-compound group, the Ind group, and the BaA group, from BaA to Cor for each of the three sources.

Condition indices were determined for different airsheds with various combinations of diesel(D), wood(W) and gasoline(G) sources and the results are shown in Table 21.

Table 21: C.I. values for normalized concentration method

<u>Source combination</u>	<u>Condition Index</u>		
	<u>9 compound group</u>	<u>Ind group</u>	<u>BaA group</u>
W / G / D	7.8	33	7.2
W ₁ / G	2.1	3.0	2.0
W ₁ / D	4.3	11	3.9
G / D	3.3	3.0	3.4

The condition indices of BaA group and 9 compound group are similar. The condition indices of Ind group are similar to those of other two groups for the W/G and G/D combinations but are much worse for the W/G/D and W/D combinations. This strongly suggests that Ind group is impractical for source identification. If we accept an

Table 18: Normalized concentration for 9-compound group

Compound	Wood		Gasoline		Diesel	
	Avg.	+- Var. (%)	Avg.	+- Var. (%)	Avg.	+- Var. (%)
BaA	0.1968	+- 70	0.0588	+- 21	0.0974	+- 36
BbF	0.1127	+- 80	0.0596	+- 21	0.1555	+- 16
BkF	0.0897	+- 95	0.0372	+- 25	0.0799	+- 16
BaP	0.1256	+- 80	0.1241	+- 49	0.0924	+- 10
Chry	0.1625	+- 66	0.0962	+- 35	0.1182	+- 19
BeP	0.0940	+- 74	0.0388	+- 24	0.0747	+- 23
Ind	0.1298	+- 86	0.0849	+- 23	0.1472	+- 32
BgP	0.0782	+- 95	0.2982	+- 20	0.1681	+- 9
Cor	0.0107	+- 40	0.2023	+- 15	0.0665	+- 8

Table 19: Normalized concentration for Ind group

Compound	Wood		Gasoline		Diesel	
	Avg.	+- Var. (%)	Avg.	+- Var. (%)	Avg.	+- Var. (%)
BbF	0.3501	+- 20	0.0868	+- 27	0.2730	+- 1
Ind	0.3181	+- 15	0.1399	+- 15	0.3068	+- 1
BgP	0.2567	+- 12	0.4595	+- 6	0.2997	+- 1
Cor	0.0751	+- 12	0.3138	+- 9	0.1205	+- 5

Table 20: Normalized concentration for BaA group

Compound	Wood		Gasoline		Diesel	
	Avg.	+- Var. (%)	Avg.	+- Var. (%)	Avg.	+- Var. (%)
BaA	0.3793	+- 13	0.0910	+- 34	0.1551	+- 19
BbF	0.3248	+- 19	0.0908	+- 23	0.3329	+- 5
BgP	0.2290	+- 16	0.4872	+- 11	0.3653	+- 4
Cor	0.0669	+- 16	0.3309	+- 8	0.1466	+- 1

error of 50%, the possible ratios of two source combinations using the 9-compound group and the BaA group are shown in Figure 10. The possible ratios for three sources are shown in Figure 11. Test data are attached as Table 22 and 23.

To study source contributions for ambient particulate control, estimated PAH contribution in normalized concentration method have to be transformed by dividing the factor of PAH content per unit particle mass ($R(j)$ expressed as equation [4]). Based on the source profiles in Table 4 and 5, the ratios of the factors among three sources, i.e. $R(W)$, $R(G)$, and $R(D)$, are 4.5:1.7:1 for 9 compounds group and 5.9:2.5:1 for BaA group.

In Figures 10 & 11, the values of acceptable condition are presented. The 9 compound group and BaA group give similar acceptable ratio ranges for two source combinations. Although the upper limit for the BaA group is always lower than 9 compounds group, the range factors, defined to be the ratio of the upper limit to the lower limit, are similar. The range factors for the normalized concentration and concentration method are compared in Table 24. In the combination of three sources, the BaA group gives a wider acceptable range than 9 compound group does. But the ratio of gasoline to diesel has to be less than 1.6, and the ratio of wood to diesel must be in the range of 0.03 to 0.3. According to Javitz et al. (1988), however, the ratio of gasoline to diesel vehicular particle emissions was 2 in the

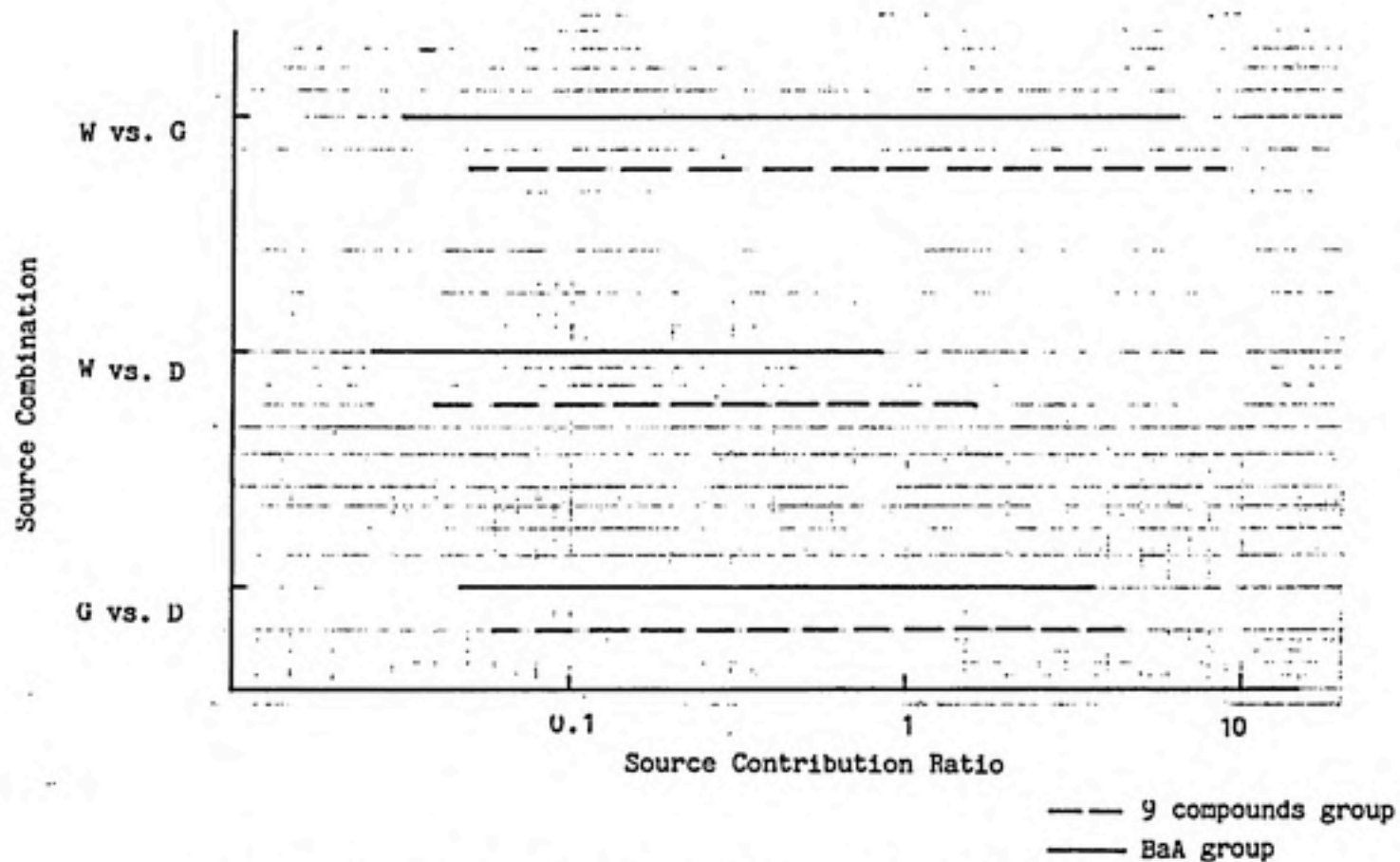


Figure 10 : Normalized Concentration Acceptable Range
at 2 Source Combination

Table 22.2: Acceptable condition test with BaA group
normalized concentration method
(Two source combination)

Contribution Ratio				AAE (%)		D
W	:	G	:	W	G	D
25		1		6	70	
20		1		6	60	
10		1		6	37	
5		1		6	23	
1		1		9	11	
0.2		1		25	7	
0.1		1		40	7	
0.05		1		60	8	
10			1	10		79
5			1	10		50
1			1	18		18
0.2			1	43		9
0.15			1	52		8
0.1			1	71		8
	10		1		9	57
	8		1		9	46
	5		1		9	32
	1		1		13	13
	0.2		1		35	9
	0.15		1		43	9
	0.1		1		59	8

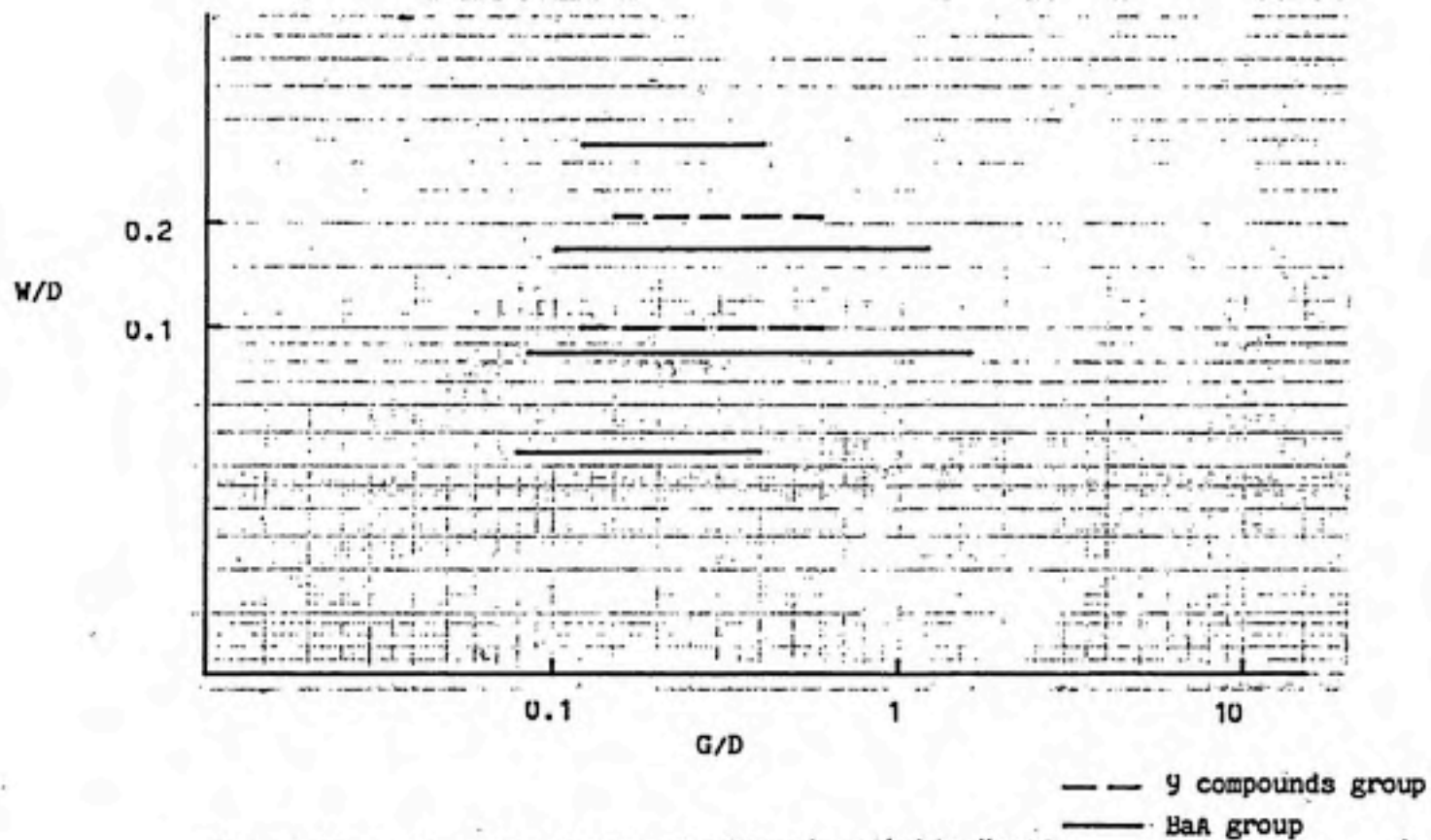


Figure 11 : Normalized Concentration Acceptable Range
at 3 Source Combination

Table 23.1: Acceptable condition test with 9-compound
group normalized concentration method
(W/G/D three sources)

Contribution Ratio			AAE (%)		
W	G	D	W	G	D
2	1	1	32	28	72
2	0.5	1	32	40	64
2	0.25	1	30	64	54
1	2	1	42	19	57
1	1	1	37	24	49
1	0.5	1	37	32	45
1	0.25	1	35	52	41
0.5	2	1	60	17	43
0.5	1	1	54	20	36
0.5	0.5	1	48	28	32
0.5	0.25	1	46	44	29
0.5	0.2	1	44	50	28
0.25	1	1	76	19	28
0.25	0.5	1	68	26	24
0.25	0.25	1	60	36	22
0.25	0.1	1	56	76	20

Table 23.2: Acceptable condition test with BaA group
normalized concentration method
(W/G/D three sources)

Contribution Ratio			AAE (%)		
W	G	D	W	G	D
4	1	1	13	33	73
4	0.5	1	12	50	63
2	2.5	1	21	16	63
2	1	1	18	26	51
2	0.5	1	16	40	43
2	0.25	1	29	60	38
1	5	1	40	12	62
1	2.5	1	30	14	48
1	1	1	24	22	38
1	0.5	1	21	32	32
1	0.25	1	19	52	27
0.5	5	1	62	12	54
0.5	2.5	1	46	13	39
0.5	1	1	34	19	29
0.5	0.5	1	32	28	25
0.5	0.25	1	28	44	21
0.5	0.2	1	28	50	20
0.25	1	1	52	18	24
0.25	0.5	1	48	26	21
0.25	0.25	1	44	40	18
0.25	0.2	1	44	46	17
0.25	0.1	1	44	74	16
0.1	1	1	100	17	21
0.1	0.5	1	87	26	17
0.1	0.1	1	85	73	14

Portland, Oregon, metropolitan area in 1983. The typical ratio between gasoline and diesel vehicular emissions might be 2 or higher in the United States. Thus, it is difficult to find an area where the ratio meets the predetermined range. We will thereafter focus on a two sources identification.

This analysis strongly suggests that the techniques developed in this paper are most applicable to the separation of two sources like gasoline and diesel or wood and gasoline or diesel and wood. There are however many instances where an airshed is impacted primarily by two sources.

Table 24 : Range factor for concentration method
and
normalized concentration method

<u>Source Combination</u>	<u>Range Factor</u>		
	<u>Concentration Method</u>	<u>Normalized concentration Method</u>	
	9 compound	9 compound	BaA group
G / D	23	73	75
W / G	50	178	200
W / D	10	40	33

Compared to the concentration method, the normalized concentration method produces smaller condition indices according to Table 24, and also gives a wider acceptable ratio range (wider by factor of 3 to 4). This means that

the normalized concentration method can be applied over a wider range of ambient conditions.

The advantages of normalized concentration method are (1) better source pattern recognition, (2) less profile variation, and (3) wider acceptable conditions. The disadvantages, however, are (1) it is difficult to combine with the concentration method because the two methods calculate different results (S_j and S'_j). In the examples presented in this study the model with the normalized concentration method calculates the individual PAH contribution from each source. The concentration technique calculates the particulate contribution from each source. It is difficult to combine with tracers which are usually used in the concentration method because the high concentration of typically used elemental tracers. Normalizing source profile with both PAH and high concentration elemental tracers, the uniqueness of PAH source pattern will decrease. (2) a final calculation is required when source contribution is concerned, i.e. transform S'_j to S_j . Here an average source intensity must be assumed to convert PAH/source to particulate/source.

To apply the methods developed in this study to real conditions, it is necessary to understand the limitations implicit in these methods. The basic assumption for sources separation is that the sources, which we are interested in, are the predominant PAH contributors, i.e. no other PAH

contributors are in the receptor site. Since PAH may be emitted from other sources, such as incinerator, fuel oil combustion, and petroleum refinery, the application of our PAH receptor model should avoid selecting the areas where these sources are significant contributors to the ambient particulate and PAH concentrations.

For the gasoline and diesel combination, according to the results in this paper, two sources can be distinguished by the normalized concentration method with PAH tracers when the source contribution ratio (G/D) is in the range of 4 to 0.05 (Figure 10). Thus, two criteria are required for using this approach effectively. The first one is that there are no significant PAH contributors in receptor site except gasoline and diesel emissions. The second one is the concentration ratio should be in the range of 0.05 to 4.

For example, in S.PALO, Brasil, 23-38% of TSP results from vehicular emissions. Other PAH sources, such as oil boiler emissions, are less than one-tenth of vehicular emissions (Alonso 1989). Thus, the PAH receptor model may be used here for automotive emissions identification. Another example, Taipei, the cultural and economic center of Taiwan, Republic of China, may be also suitable for this method, since the vehicular emissions are the major man-made pollution source and there are less industrial PAH emission sources. The contribution ratio between gasoline and diesel exhausts may be no more than 2 due to the fact that public

transportation with diesel buses play an important role in city transportation. In the United States, many urban and suburban areas may use this approach to identify gasoline and diesel vehicular emissions in the summer season.

In winter, residential wood combustion contribute considerable amount of PAH in many northern American cities. Figure 10 shows that residential wood combustion and gasoline exhaust can be differentiated when the W/G ratio is in the range of 0.5 to 9. A study of wood combustion impact in Portland, Oregon (Cooper 1980) shows that 51% of respirable particles result from wood combustion. The ratio of wood to gasoline emissions may be in the range of 5 to 10. Thus the PAH model can be useful in this area for source identification. Meanwhile, wood combustion and diesel exhaust can be separated when W/D ratio is in the range of 0.04 to 1.6, if there are two sources only.

Since, gasoline and diesel exhausts always exist in the same area, dividing them into two combinations, wood and gasoline or wood and diesel combinations, is not practical. A method, which is used in a case study as shown later, overcomes this problem by using a mixture of gasoline and diesel to represent the vehicular source. The proportion in the mixture is determined from studies conducted during summer.

CMB modeling assuming reactive PAH

The CMB model with assuming inert PAH tracers was examined in the first step. The general conclusion was that the neither the concentration method nor normalized concentration method can not offer reasonable source separation for the three combustion sources of wood, gasoline and diesel, but the separation of two sources combinations can be applied conditionally. Therefore, we focused on two sources identification in the second step.

Because PAHs are degradable during atmospheric transport, source profiles will be a function of decay time. A decay factor is included in the mass balance equation to interpret the concentration change.

The revised mass balance equation is given by

$$C(i) = \text{SUM}(S(j) * F(i,j) * \alpha(i,j)) \quad [6]$$

where $C(i)$, $F(i,j)$, $S(j)$ have the same meaning as the parameters used in equation [1]. And $\alpha(i,j)$ is decay factor of compound i for source j .

In the normalized concentration method, the mass balance equation is given by

$$C(i) = \text{SUM}(S'(j) * NF'(i,j)) \quad [7]$$

$$\text{where } NF'(i,j) = \frac{F(i,j) * \alpha(i,j)}{R'(j)}$$

$$R'(j) = \text{SUM}(F(i,j) * \alpha(i,j)) \quad i=1, 2, \dots, n.$$

Chamber model

The concept of the chamber model is that source emissions are injected into and aged in a closed system. Different source emissions may be injected at different times, but each source is allowed to be injected only once. Therefore, each source emission has a specific decay time until sampling. First order decayed source profiles can represent the source signatures at the sampling time. The decay factor, $\alpha(i,j)$, for chamber model will be

$$\begin{aligned} \alpha(i,j) &= \frac{C_i(t(j))}{C_i(t=0)} \\ &= \text{EXP}(-k(i) * t(j)) \end{aligned}$$

where

$K(i)$: decay constant for compound i

$t(j)$: decay time for source j

To evaluate the CMB model with the addition of PAH decay constants, a test data set is needed. To generate this data set, a captured atmosphere in an enclosed box or an outdoor chamber is assumed. Different dilute mixtures of known diesel, wood, and gasoline combustion particles are added to the chamber. Under natural sunlight, PAHs are allowed to decay according to first order kinetics. The

environmental parameters in the chamber are used to estimate the decay constant (Kamens et al. 1988).

Sets of data were generated by combining decayed source profiles with known decay times. Least square fitting with concentration and normalized concentration method was then undertaken using source profiles with different decay time combinations. Two indicators are used to estimate the correct decay time. They are chi-square and the estimated mass contribution.

The following example illustrates the process. The 4 compounds, BbF/BkF/BaP/BgP, in wood and gasoline combustion particles were aged in the chambers. In this example, wood PAH were aged for 120 minutes and gasoline soot particles were aged for 60 minutes before the air in the chamber arrives at the receptor site. Forty percent of the mass of particles come from wood combustion and 60% is from gasoline exhaust. The total suspended particles are assumed to be 100 ug/m^3 . In order to avoid exact matching, the PAH receptor concentrations were treated with 10% change for each compound in opposite directions, and 25% variations in source profiles were used in CMB model calculation. The first step in the analysis was to fix one source with a fresh source profile and then vary the decay time for the other source. Results for the first step are shown below in Table 25.

When fresh wood soot emission was used, chi-square

values were improved by increasing the aging time of gasoline soot PAH up to 120 minutes. But, the mass contributions showed that the calculated TSP was overestimated when the aging time of gasoline increased to 90 minutes. Holding gasoline emission to a fresh source profile gave the lowest chi-square when wood soot aged from 120 to 180 minutes. The results suggest either 120 or 180 minutes as the aging time of wood soot and a possible decay time under 90 minutes for gasoline soot.

In the second step, wood combustion PAH were aged for 120 and 180 minutes and gasoline were aged from 0 to 90 minutes. Results are shown in Table 26.

Table 25: The results of the first step chi-square test

<u>decaying time</u> (min.)		<u>mass contribution</u> (ug/m ³)		Chi-square
wood	gasoline	wood	gasoline	
0	0	3.66	23.17	35.15
0	30	3.12	45.20	32.15
0	60	2.85	90.26	24.10
0	90	2.88	152.00	17.79
0	120	2.71	277.00	11.33
60	0	14.73	18.65	14.32
120	0	39.56	20.26	2.78
180	0	80.38	24.77	2.19
300	0	247.00	31.20	9.53

Table 26: Results of the second step chi-square test

<u>decaying time</u> (min.)		<u>mass contribution</u> (ug/m ³)		Chi-square
wood	gasoline	wood	gasoline	
120	30	38.45	36.74	3.32
120	60	37.51	65.40	1.32
120	90	35.00	117.00	1.31
180	0	80.38	24.77	2.19
180	30	75.30	44.90	2.74
180	60	70.50	81.70	3.67
180	90	66.00	139.00	5.72

Chi-square values show that two selections might be correct, that is 60 min. for gasoline and 120 min. for wood or 90 min. for gasoline and 120 min. for wood. The second choice, however, produced results in which 35% of the mass came from the wood and 117% from gasoline. Hence, the total mass contribution was overestimated by 50%. These results suggest that the best combination comes from the lowest chi-square value and one in which mass is conserved. The magnitude of error depends on adequate fitting elements selection, variations of source emissions, and measurement error.

A major difficulty with the above two-step method is that it requires data for mass contributions, which are not available for atmospheric samples. Therefore, an attempt was made to deduce the aging time only on the basis of chi-square. The concentration method and normalized concentration method with 9 PAH compounds were used to examine the feasibility for the determination of aging time

using only chi-square. A computer program was written (Appendix B) to calculate the chi-square value for all combinations and yield a chi-square matrix as output.

Based on the 9 compounds average source signature, displayed in Table 4 & 5, a data set was generated using the same source combination and the same data treatment as those in the previous example. The chi-square values for the concentration method were calculated with chi-square testing program described in Appendix B. The chi-square matrix is given in Table 27. It shows that the chi-square value decreases when the aging time increases and no optimum chi-square value exists. The results indicate that the decay times can not be determined only with chi-square criteria when concentration method is used.

The normalized concentration method was also used to test this data set, and the resulting chi-square matrix is given as Table 28. A minimum chi-square value is obtained at 150 minutes decay for wood PAH and 45 minutes for gasoline. The estimated source contributions were 51.2 $\mu\text{g}/\text{m}^3$ for wood and 52.3 $\mu\text{g}/\text{m}^3$ for gasoline. The errors are 28% for wood and 13% for gasoline. These results show the chi-square criteria can be used independently for source decay time selection when the normalized concentration method is used. Therefore, the normalized concentration method may be a better choice for the ambient studies.

Table 27: Chi-square matrix with concentration method

Wood	Gasoline Aging Time (minutes)							
	30	45	60	90	120	150	180	210
30	9.52	5.03	2.68	1.01	0.63	0.48	0.37	0.26
45	5.99	3.31	1.79	0.75	0.57	0.48	0.38	0.28
60	3.40	1.94	1.09	0.59	0.57	0.53	0.43	0.32
90	1.01	0.57	0.39	0.50	0.69	0.70	0.58	0.43
120	0.32	0.18	0.20	0.50	0.77	0.82	0.71	0.54
150	0.12	0.09	0.14	0.45	0.75	0.84	0.76	0.60
180	0.06	0.06	0.11	0.37	0.64	0.76	0.73	0.61
210	0.04	0.04	0.09	0.27	0.49	0.62	0.63	0.56

Table 28: Chi-square matrix with normalize concentration method

Wood	Gasoline Aging Time (minutes)							
	30	45	60	90	120	150	180	210
30	3.23	2.52	2.00	1.67	2.08	2.78	3.49	4.07
45	2.20	1.66	1.30	1.19	1.73	2.51	3.25	3.79
60	1.56	1.12	0.86	0.96	1.65	2.55	3.34	3.99
90	0.84	0.54	0.45	0.92	2.01	3.27	4.37	5.21
120	0.49	0.31	0.37	1.24	2.84	4.60	6.11	7.23
150	0.33	0.24*	0.45	1.74	3.87	6.20	8.22	9.72
180	0.29	0.30	0.62	2.28	4.92	7.84	10.27	12.34
210	0.30	0.38	0.82	2.82	5.88	9.35	12.32	14.67

Ambient model

In the ambient atmosphere, particles are collected with different decay signatures at the receptor site because wood, diesel, and gasoline emissions come from area sources. However, an area source j can be represented as an aggregate of a large number of point sources q . For such an aggregate, the concentration of compound i contributed by area source j at the receptor site can be expressed as

followed.

$$C(i,j) = \text{SUM}(S(q) * F(i,j) * \text{EXP}(-K(i) * t(q))) \quad q=1 \text{ to } r$$

where $C(i,j)$ is the concentration of component i contributed by area source j . $S(q)$ is the source contribution of each individual point source, and is composed by total number of r individual point sources.

If source j is a single point source, the $C(i,j)$ will be

$$C(i,j) = S(j) * F(i,j) * \text{EXP}(-K(i) * t(j))$$

Because the area source expression can not be simplified to a single point source expression, i.e. a first order decay function of an average decay time. Therefore, the decay factor in the chamber model cannot be directly transferred to the ambient atmosphere. Friedlander (1981) suggested that a continuous stirred tank reactor (CSTR) model, in which reactants introduced into the CSTR immediately reach a uniform concentration, can be used to interpret the source mixing phenomenon. The decay factor been used in equations [6] and [7] is given by

$$\alpha(i) = 1 / (1 + K(i) * \theta)$$

where: θ : the average residence time in CSTR

$K(i)$: decay constant for compound i

Case studies

The data from two studies (Miguel et al. 1989, Sexton et al. 1985) were used to test the CMB PAH model with CSTR decay factor. In these two studies, ambient PAH data were taken and source apportionment were estimated by CMB techniques with different tracers. One study investigates the combination of gasoline and diesel emissions, and the other investigates a combination of wood combustion and vehicular emissions. Since the normalized concentration method provides an effective source pattern identification and residence time determination, This method was examined with PAH data shown in these two studies. The source patterns for three combustion sources were characterized in previous section with PAH data from chamber studies and are listed in Tables 4 and 5.

To calculate PAH decay constants, one needs to know the average solar intensity in $\text{cal/cm}^2\cdot\text{min}$ and the water vapor concentration (Kamens et al. 1988). Because these data were not directly available, these parameters were estimated from other sources. The residence time was first determined by minimizing chi-square in the chi-square test. The mass contributions were then calculated with source profiles and selected residence time.

Vehicular impacted airshed

Data for the first case, named case 1, was obtained

from the Rio de Janeiro aerosol characterization study of Miguel et al. (1989). The site was located in the neighborhood of a mixed residential-commercial area and was influenced by heavy traffic. All 12-hour TSP samples were collected with a Hi-Vol sampler using quartz fiber filters. Automotive source samples were collected in tunnel test. PAH compounds, elemental carbon (EC) and volatilizable organic carbon (VOC) were analyzed with HPLC and thermal evolution method. The vehicular emission was acknowledged to be the major source of particulate PAHs, because the receptor site and tunnel had similar PAH concentration patterns and the same PAH ratios (i.e. BaA to BaP, BkF to Ind, and BgP to Ind.) existed in the tunnel and ambient samples. Different kinds of tracers were used in the Miguel et al.'s study to estimate vehicular contribution. They estimated vehicular contribution to be 24% with EC and VOC tracers. This agreed with a contribution, 21%, obtained when they used BkF, BgP and Ind as tracers. However, when Miguel et al. used BaA or BaP as tracer they underestimated the vehicular contribution. Data presented in this study strongly suggest that the underestimation can be attributed to chemical degradation since BaA and BaP are very reactive. Because the PAH are contributed predominantly by automobile emissions in this case, the ambient model with normalized concentration method may be used to differentiate gasoline and diesel exhausts.

For the data in case 1, we assumed a 12 hours average solar intensity of $1 \text{ cal/cm}^2\text{min}$ because in southern America like Florida the 24 hours average solar intensity was 0.3 to $0.4 \text{ cal/cm}^2\text{min}$ in winter (Ruffner and Bair 1981). The water vapor concentration was assumed to be $10 \text{ g H}_2\text{O/m}^3$ because the average temperature during sampling period was 21.5°C . Decay constants were then calculated with these parameters. Measured PAH and calculated PAH at receptor site are shown in Table 29. Seven PAH compounds are used for the differentiation of gasoline and diesel. The source signatures shown in Table 5 were used. To determine the residence time, chi-square values were calculated with 8 residence times, between 0 and 300 minutes. Table 30 shows chi-square values and estimated source contributions for each residence time.

According to Table 30, the minimum chi-square value occurs at 30 minutes. The short residence time indicates that the source profiles have a near fresh compositional signature. This may explain why the results using carbon tracers are closely consistent with the results using BkF/Ind/BgP tracers. This gives an estimated PAH contribution from both gasoline and diesel of 10.94 ng/m^3 . The measured PAH was 10.23 ng/m^3 , and the difference from the estimation is 7% only. The calculated PAH concentrations shown in Table 29 were calculated as the sum of all the products of PAH concentration from each source

and the corresponding source signature.

The PAH source signature of 30 minutes residence time was then used to calculate source contributions. The source contribution are 11.66 ug/m^3 for gasoline engine exhaust, and 2.62 ug/m^3 for diesel engine exhaust. The comparison of results are shown in Table 31. The PAH concentration (i.e. total mass concentration of 7 PAH compounds) for the CMB results by Miguel et al. (1989), are calculated as the sum of the product of source contribution and tunnel's PAH profile.

The CSTR model results for the 7 PAH tracers are in good agreement with the measured PAH contribution for the same 7 PAH tracers. A value of 17.3% of the TSP was estimated for vehicular emissions using this technique. This is lower than the 24% contribution obtained from carbon tracer method, or 21% from BkF, BgP, and Ind tracers method. The reason for the difference may be the existence of 10 to 20 percent of ethanol vehicular fleet at the site. Ethanol vehicular emission can not be predicted with gasoline or diesel emissions, but the source profile obtained from tunnel tests can predict the signature including ethanol vehicles.

The ratio of gasoline vehicles contribution to diesel vehicles is 4.45 by CSTR model. Considering the 70-80% of gasoline and 8-10% diesel vehicular fleet at the site, the ratio may be reasonable because of the high emissions for

diesel vehicles.

Table 29: Case 1 PAH concentrations at receptor site and calculated results**

PAH	<u>Receptor site</u> (ng/m ³ +- SD)		<u>Calculated</u> (ng/m ³)
BaA	0.53	+- 0.224	0.76
Chry	1.17	+- 0.498	1.70
BbF	1.18	+- 0.420	1.28
BkF	0.51	+- 0.163	0.67
BaP	1.35	+- 0.571	1.45
BgP	3.75	+- 1.24	3.69
Ind	1.74	+- 0.546	1.39
Total PAH =	10.23		10.49
*EC	7280		
VOC	6840		

* EC : elemental carbon

VOC : volatilizable organic carbon

** the calculated results based on normalized concentration method with reactivity correction based on CSTR model

Table 30: Result of case 1 chi-square test

<u>Residence Time</u> (min.)	<u>PAH Contribution**</u> (ng/m ³)		<u>chi-square</u>
	Gasoline	Diesel	
0	7.88	3.17	0.010
15	8.25	2.73	0.0074
30	8.57	2.37	0.0069 *
60	9.05	1.82	0.0080
120	9.63	1.15	0.0095
180	9.97	0.76	0.011
240	10.19	0.51	0.011
300	10.12	0.71	0.013

* minimum chi-square

** total of 7 PAH compounds

Table 31: CSTR model result comparison

Source	Tracer used	PAH(7 compounds) Contribution (ng/m ³)	Source Contribution(%) (ug/m ³)
CSTR model	BaA, Chry, BbF, BkF, BaP, BgP, Ind.	10.94	14.28 (17.3) (G : 11.66 D : 2.62)
Miguel(1989)	BbF, BgP, Ind	12.06	17.6 (21)
	VOC, EC	13.70	20.0 (24)
	BaP	7.13	10.4 (13)
	BaA	7.33	10.7 (13)
measured		10.23	*

* average measured TSP loading = 82.6 ug/m³

Wood smoke impacted airshed

Data for the other case, case 2, was obtained from a wood-burning community aerosol study in Waterbury, Vermont (Sexton et al. 1985). The community of Waterbury is mostly residential, with no large industrial sources and few commercial establishments of any size. Within residential sections of Waterbury, wood combustion is likely to be the major source of winter aerosol. The study was conducted to estimate the impact of wood combustion from January to March 1982. All 24-hour Hi-Vol particulates samples were collected on quartz filters for PAH analysis with GC/MS. Dichotomous particulates samples were collected on Teflon filters for elemental constituents determination with an X-ray fluorescence spectrometer. In this study, the contribution of vehicular emissions, 2.3 ug/m³, was

determined by a single element, Br, in the CMB model. The impact of wood combustion, $10-16 \text{ ug/m}^3$, was obtained by the authors from the total mass of fine fraction by subtracting the vehicular contribution and the impact of pollutant transport from upwind sources. Meanwhile, factor analysis was carried out to develop factor patterns from elemental data. Factor 1 was significantly related to K, Br and Pb. This factor appears to be dominated by contribution from wood burning and automotive exhaust. Using this factor pattern, at least 70% of the variance in individual PAH concentrations can be explained. Therefore, local sources, i.e. residential wood burning and automotive emissions, are the major determinants of ambient PAH concentrations in Waterbury.

In the analysis of this study, a combination of three sources, i.e. wood combustion, gasoline and diesel engine exhaust was used. Source signatures for these three sources shown in Tables 4 and 5 were used. Since our model does not work well with all three of these sources, gasoline and diesel engine exhausts were combined into one category called vehicular exhaust. This gave only two sources. Based on the study in Portland, Oregon (Javitz et al. 1988), the ratio of gasoline to diesel engine exhaust is assumed to be 2. Vehicle source profile was generated by adding the profiles of gasoline engine exhaust and diesel engine exhaust with the ratio of 2.

The average temperature was -7°C during the study. According to Ruffner and Bair (1981, 1985), the average relative humidity (RH) in Vermont was 60-70% from January to March, and the average solar intensity in the winter was 61 W/m^2 at Caribon, Maine; and 66 W/m^2 at Boston, Mass.. Therefore, 65% RH or $1.9 \text{ gH}_2\text{O/m}^3$ at -7°C , and $0.1 \text{ cal/cm}^2\cdot\text{min}$ as an average solar intensity were selected. The solar intensity was the average of the dark and light hours. The decay constants of PAHs were calculated with these meteorological parameters and are listed in Table 32. The concentration of measured PAH and the corresponding estimated PAH are listed in Table 33.

Table 32: PAHs decay constant for case 2 study

<u>PAH</u>	<u>decay constant (1/min.)</u>
BaA	0.000436
BaP	0.000456
Chry	0.000129
BeP	0.000129
Ind	0.000061
BgP	0.000133
Cor	0.000061

Table 33: Case 2 PAH concentration

<u>PAH</u>	<u>Concentration (ng/m³)</u>			
	<u>measured</u>			<u>calculated</u>
BaA	1.2	+-	0.26	1.21
BaP	0.8	+-	0.16	0.82
Chry	1.9	+-	0.43	1.45
BeP	0.9	+-	0.27	0.83
Ind	1.0	+-	0.29	1.30
BgP	1.0	+-	0.27	0.96
Cor	0.3	+-	0.08	0.31
Total PAH =	7.1			6.88

Seven compounds, BaA, BaP, Chry, BeP, Ind, BgP, and Cor, were used for the least square fitting. Table 34 shows the chi-square values for residence time up to 2520 minutes. The chi-square value reaches its minimum at 1560 minutes. This gives an estimated PAH concentration from both sources of 6.88 ng/m^3 . The total measured PAH was 7.1 ng/m^3 , and the difference between measurement and estimation is 3%. The estimated source contributions are 9.64 ug/m^3 for wood combustion, and 1.04 ug/m^3 for vehicle emission. The comparison of results are shown in Table 35.

Table 34: Case 2 chi-square test results

Residence Time (minutes)	PAH Contribution (ng/m^3)		chi-square
	Wood	Vehicle	
0	5.76	1.37	0.0292
840	5.93	1.09	0.0135
1080	5.93	1.04	0.0120
1320	5.93	1.00	0.0112
1560	5.91	0.96	*0.0109
1800	5.89	0.94	0.0111
2040	5.87	0.92	0.0117
2280	5.84	0.90	0.0124
2520	5.81	0.88	0.0134

* minimum chi-square

Table 35: Case 2 result comparison

Source	Tracer used	7 PAH Contribution (ng/m ³)		Source Contribution (ug/m ³)	
		W*	V	W	V
CSTR model	BaA, BaP, Chry, BeP, Ind, BgP, Cor	5.91	0.96	9.64	1.04
Sexton(1985)	Br 1-others	7.10(total)		10-16	2.3

* W: residential wood combustion
V: vehicular emissions

Table 32 shows that the reactivity of PAHs are very low. Therefore, the estimated PAH contributions, obtained from the signatures with residence time of 1560 minutes, are not significantly different than those from fresh signature. The results suggest that fresh signature may be used for source separation in the winter time like the situation in case 2. The least square fitting with PAH compositional signatures is in good agreement with the measured data. The source contributions from CSTR model are lower than those from Sexton's method. Possible reasons for the difference are as follows: (1) The emission intensity is a site dependent parameter. The higher emission intensity used in source profiles will yield an underestimation. The emission intensity for wood combustion have been corrected to 1/4 of

the intensity from chamber studies. But, a full knowledge of the site still is crucial for sources identification.

(2) Basically, the CSTR model is equivalent to a simple atmospheric box model with fixed inversion lid (Friedlander 1981). Usually the inversion heights and wind speeds are different at day time and at night. Meanwhile, the vehicle emissions are usually emitted more at rush hours in the day time, and residential wood combustion sources emissions are highest at night. Thus, the 24 hours sampling may contribute to the disparity between measurement and estimation. (3) Meteorological parameters are influential in CSTR modeling. Usually, the absolute humidity may not make a large change over 24 hours sampling period, but sunlight intensity does.

The CSTR model is not very accurate for 24-hour sampling periods because the diurnally varying solar intensity must not be represented as a single 24-hour average. In the case study, if we use $0.2 \text{ cal/m}^2\cdot\text{min.}$ instead of 0.1 , the decay constant of BaP change from 0.000456 to 0.000886 . The source contribution change from 9.64 ng/m^3 contributed by residential wood combustion to 9.68 ng/m^3 . The change for vehicular emissions would be from 1.04 ng/m^3 to 1.21 ng/m^3 . In addition, if we assumed that wood soot was generated primarily at night and vehicular soot was generated during day, a solar intensity of $0.1 \text{ cal/m}^2\cdot\text{min.}$ for wood and $0.4 \text{ cal/m}^2\cdot\text{min.}$ for vehicles

were used. We obtained 9.6 ug/m^3 for wood and 1.49 ug/m^3 for vehicles. This shows that the contributions from wood combustion are almost the same, and the contribution of vehicle exhaust increase with higher solar intensity. This may mean that vehicle exhaust predominantly incline to be exposed to higher sunlight intensity. Therefore, the emission intensity may be the main reason for the difference of wood contribution, and the difference of vehicles contribution may be attributed to emission intensity, the ratio of gasoline to diesel, and sunlight intensity.

The results from the two case studies indicates that the method of using normalized PAH source signatures can provide a reasonable source pattern differentiation for combustion sources. The characterized source patterns and sufficient meteorological parameters are two essential parameters. Good estimation of source contributions are, however, strongly influenced by using representative emission intensities. The method of combining gasoline and diesel exhausts into one category can be a practicable technique in the condition of wood smoke impacted airshed.

V. SUMMARY AND CONCLUSION

Condition index and CMB performance testing program provide a technique of tracer selection. In PAH compounds, the BaA group and the 9 compound group as tracers in CMB model gave similar performance for combustion sources identification. In the combinations of two sources (W/G, G/D, and W/D), reasonable working ranges were provided by these two group. Unfortunately, the three sources combination can not be separated effectively with these two groups of PAH tracers.

Source characterization indicated that PAH emissions from combustion sources can be characterized as a basic source pattern with different emission intensities. The performance of CMB model with PAH tracers can be improved by using these characterized source patterns in terms of normalized concentration method.

When PAH reactivity was introduced, a CMB model with CSTR decay factor was used to improve model predictions. The residence time was firstly determined by chi-square minimizing method using the normalized concentration method. The source contributions were then calculated. This approach was examined with two case studies.

The results of case study 1 showed a reasonable separation of gasoline and diesel fueled vehicles. The difference of 4% in calculated vehicular contribution from the results by Miguel et al. (1989) can be attributed to 10 to 20 percent of ethanol fueled vehicles fleet at the site which cannot be predicted effectively by gasoline or diesel fueled emission pattern.

In a second case study, which was impacted primarily by wood and gasoline emission, the estimated contributions from CMB model were lower than those predicted by Sexton et al. (1985). Two possible reasons for the difference are: (1) emission intensity: The intensity for residential wood combustion derived from chamber studies does not reflect the PAH source signature in this area. An improvement of source signature by modifying this signature of chamber studies with data from other ambient studies gave a more reasonable result which was closer to the predictions by Sexton et al. (1985). Thus, the site dependent parameter, emission intensity, has to be carefully considered. (2) A 24 hour average solar intensity may not be adequate for vehicular emissions which are emitted predominantly during day time. This suggests that shorter sampling periods are needed.

In general, the CMB normalized concentration method with the CSTR model gave reasonable predictions in two case studies. This shows PAH tracers can be useful in CMB model to identify combustion sources.

VI. RECOMMENDATIONS

The combustion sources differentiation and contribution identification using PAH tracers are effective for combinations of two sources under some conditions. Meanwhile, case studies show that the normalized concentration method with CSTR decay factor can be effective for ambient studies in the condition of two sources. To improve model prediction with organic tracers, it is recommended that the following works should be necessary.

1.) Source characterization

To enable more sources to be resolved in organic receptor modeling, the source signatures must be identified not only with PAH compounds but also with additional organic compounds including alkanes, oxy-PAH, or other derivatives of PAH. For example, C-20 alkane have been found in diesel exhaust but not in wood combustion. Inclusion of this compound in the CMB model would probably enable 3 sources in the gasoline, diesel and wood smoke group to be resolved. Derivatives of PAH such as oxy-PAH or nitro-PAH which are more stable than PAH, may be used as source signature (Kamens et al. 1987, 1989). Meanwhile, Daisey et al. (1986)

indicated that 6-nitro-BaP might be useful in tracing motor vehicle emissions because the concentrations of 6-nitro-BaP in vehicle emissions were about an order of magnitude higher than those obtained from wood burning and a coal-fire boiler.

2.) Better decay constant estimation

It is inevitable to include decay constant information in organic receptor modeling. A good estimation of the decay constants, which are used to describe the degradation of organic compound under natural atmosphere and different substrates, is important for effective model prediction.

3.) Adequate samples

Combustion aerosols predominantly belong to the sub-micron size range. Taking samples in this size range will eliminate the high contributions from geological materials and help us concentrate more on combustion sources.

To reduce the error caused by averaging sunlight intensity over 24 hours periods, taking day time samples and night time samples separately is recommended.

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APPENDIX A

```

/* D:\GAUSS\REG\simulate */
/* Data simulate with combustion sources PAHs tracer for
CMB model */
/* simulation base on log normal distribution */

n=100;
seedx=123; seedb=456; seedy=789;
output file = simtest.out reset;

/* x matrix : source profile */
/* svx      : standard variation (%) of x */
loadm xo[9,3]=pahcon.dat;
loadm svxo[9,3]=vpahcon.dat;
/* r : no of elements to be used */
/* c : no of source to be used */
r=9; c=3;      let s[3,1]=0 0 0 ;          /* s[c,1] */
                let ss[3,1]=0 0 0;
rownum=1|2|3|4|5|6|7|8|9;
colnum=1|2|3;
x=submat(xo,0,0);
                                print " source profile x= " x;

lnx=ln(x);
scx=sumc(x)';
svx=submat(svxo,0,0);
                                print " CV of X =" svx;

stdx=x.*svx;
sstdgx=ln(svx^2 +1);
lnmx= lnx-0.5*sstdgx;
stdgx= sqrt(sstdgx);

/* b matrix : source contribution */
/* svb      : standard variation (%) of b */

loadm bo[3,1]=pahb.dat;
loadm svbo[3,1]=pahvb.dat;
rnum=1|2|3;                                /* no.=c */
b=submat(bo,0,0);
                                print "source contribution b=" b';

lnb=ln(b);
svb=submat(svbo,0,0);
stdb=b.*svb;
                                print "CV of B = " svb';
sstdgb=ln(svb^2+1);
lnmb=lnb-0.5*sstdgb;
stdgb=sqrt(sstdgb);

/* Simulate correlated source contribution */

loadm covm[3,3]=datavar;
selrnum=1|2|3;

```

```

        selcnum=1^2^3;
        covm=submat(covm,0,0);
        sigma=stdgb.*(stdgb'.*covm);
        y=chol(sigma);
        a=y';
        z=rndns(c,n,seedb);
        v=lnmb+a*z;
        sbu=exp(v);

/* Load CV of Y */
        loadm svyo[9,1]=convy.dat;
        svy=submat(svyo,0,0);
/* Monte Carlo simulation */
        i=1; do until i>n;
/* create 95% C.I. random number matrix for x simulation */

        xnumber=0; xmatrix=0;
        do until xnumber>r*c;
            u=rndns(1,1,seedx);
            if abs(u)<1.96; xmatrix=xmatrix|u;
                           xnumber=xnumber+1;
            endif;
        endo;
        xmatrix=submat(xmatrix,sega(2,1,r*c),0);
        xmatrix=reshape(xmatrix,r,c);
        lnu=xmatrix.*stdgx;
        lnxu=lnmx + lnu;
        xu=exp(lnxu);
/* Normalize sum of Xi to constant */
        scxu=sumc(xu)';
        norx=scx./scxu;
        xu=norx.*xu;
/* Simulated source contribution */
        bu=sbu[:,i];
        print "simulated b=" bu';

yp=xu*bu ;

/* Simulate measurement error */

        lny= ln(yp);
        sstdgy=ln(svy^2 +1);
        lnmy=lny -0.5*sstdgy;
        stdgy=sqrt(sstdgy);
/* create 95% C.I. random numbermatrix for y
simulation */
        ynumber=0; ymatrix=0;
        do until ynumber>r;
            uy=rndns(1,1,seedy);
            if abs(uy)<1.96; ymatrix=ymatrix|uy;
                           ynumber=ynumber+1;
            endif;
        endo;

```

```

ymatrix=submat(ymatrix,sega(2,1,r),0);
ep=ymatrix.*stdgy;
my=lnmy +ep;
y=exp(my);
print "simulated y =" y';

/* solve best from simulated y with effective variance
CMB method */

stdy=(y.*svy)';
let best[3,1]=0 0 0 ;
iter=0; tol=0.01; maxiter=10; sindr=0;
do while sindr==0;
    ebest=best';
    esv=sumc(((ebest.*stdx)^2)');
    ev=esv/n+stdy^2;
    v=diagrv(eye(r),ev);
    /* v=Watson's effective variance */
    best=inv(x'*inv(v)*x)*x'*inv(v)*y;
    re=sumc(abs(best-ebest')./abs(best));
    iter=iter+1;
    if re <=tol; sindr=1; endif;
    if iter >=maxiter; sindr=1; endif;
enddo;

    sel=best .>=0;
    comp=minc(sel);
if comp == 1;
    print "best=" best';
    rr=abs(bu-best);
    rs=(bu-best)^2;
    s=s+rr;
    ss=ss+rs;
else;
    rx=selif(x',sel); rx=rx';
    stdrx=selif(stdx',sel); stdrx=stdrx';
    sindr1=0; iter1=0;
    let best[3,1]=0 0 0 ;
    best2=selif(best, sel);
    do while sindr1==0;
        ebest=best2';
        esv=sumc(((ebest.*stdrx)^2)');
        ev=esv/n + stdy^2;
        v=diagrv(eye(r),ev);
        best2=inv(rx'*inv(v)*rx)*rx'*inv(v)*y;
        re=sumc(abs(best2-ebest')./abs(best2));
        iter1=iter1+1;
        if re<=tol; sindr1=1; endif;
        if iter1>=maxiter; sindr1=1; endif;
    enddo;
    print "best2=" best2';
    k=1; j=1;
    do until k>c;

```

```
        if sel[k,1]==1;
            best[k,1]=best2[j,1];
            j=j+1;
        endif;
        k=k+1;
    endo;
    print "best=" best'; print "sel=" sel';
    rr=abs(bu-best);
    rs=(bu-best)^2;
    s=s+rr;
    ss=ss+rs;
endif;
i=i+1;
endo;
AAE=s/n;
RMSE=sqrt(ss)/n;
end;

print "avg. absolute error=" aae';
print "root-mean-square error=" rmse';
```

APPENDIX B

```

/* Chi-square test program with different decay times */
/* Input data: ambient data  ng PAH/m3 */
/*               source profile  ng PAH/ug particles */
/*               decay constants of PAH  1/min. */
/*               residence time          minutes */
/* CMB with CSTR decay factor */

```

```

n=1; output file = case27nc.out reset;
r=7; c=2;
colnum=12;
rownum=1|2|3|4|5|7|8;

```

```

/* Input source profile, decay constant, and residence
times*/

```

```

loadm xo[9,3]=pahcon.dat;
loadm ko[9,1]=deccon.dat;
loadm to[8,1]=theta.dat;
loadm svnxo[9,3]=vpah9nc.dat;
loadm svyo[9,1]=convy.dat;
      x=submat(xo,rownum,colnum);
      k=submat(ko,0,colnum);
      svnxs=submat(svnxo,rownum,colnum);
      svy=submat(svyo,rownum,0);

```

```

/* Input ambient data */

```

```

let y[7,1]= 1.2 0.8 1.9 0.9 1.0 1.0 0.3;

```

```

x1=x[.,1];
x2=x[.,2];
i=1; chimat=0;

```

```

do until i>8;
  t1=to[i,.];
  df1=1/(1+t1*k);      /* decay factor for source 1 */
  dx1=df1.*x1;
  sdx1=sumc(dx1);

```

```

/* Normalized concentration profile */

```

```

ndx1=dx1/sdx1;

```

```

j=1;

```

```

do until j>8;
  t2=to[j,.];
  df2=1/(1+t2*k);
  dx2=df2.*x2;
  sdx2=sumc(dx2);

```



```

ndx2=dx2/sdx2;

nx=ndx1*ndx2;

stdx=nx.*svnx;
stdy=(y.*svy)';

/* CMB effective least square fitting */

let best[2,1]=0 0 ;
iter=0; tol=0.01; maxiter=10; sindr=0;
do while sindr==0;
    ebest=best';
    esv=sumc(((ebest.*svnx)^2)')';
    ev=esv/n +stdy^2;
    v=diagrv(eye(r),ev);
    best=inv(nx'*inv(v)*nx)*nx'*inv(v)*y;
    re=sumc(abs(best-ebest')./abs(best));
    iter=iter+1;
    if re<=tol ; sindr=1; endif;
    if iter>=maxiter; sindr=1; endif;
enddo;

/* calculate chi-square value */

expect=sumc((best'.*nx)');
chisq=sumc((y-expect)^2./ev');
chimat=chimat|chisq;
print "source1 i.d.=" i;
print "source2 i.d.=" j;
print " b estimated= " best';
print "chisq =" chisq;
j=j+1;
enddo;
i=i+1;
enddo;

chimat=submat(chimat,seqa(2,1,64),0);
chimat=reshape(chimat,8,8);
print "chisquare matrix";
print chimat;

end;

```